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Impact of Organic Solvents on the Integrity of Clay Liners for Industrial Waste Disposal Pits Implications for Groundwater Contamination

Colorado State Univ., Fort Collins

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Robert S. Kerr Environmental Research Lab.
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FINAL REPORT ON

IMPACT OF ORGANIC SOLVENTS ON THE INTEGRITY OF CLAY LINERS FOR INDUSTRIAL WASTE DISPOSAL PITS: IMPLICATIONS FOR GROUNDWATER CONTAMINATION

BY

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This research project was aimed toward development of procedures by which to evaluate the potential for groundwater contamination by hazardous industrial wastes disposed of on land. Studies were conducted to describe the attenuative properties of the soil, soil permeability, and the effects of a number of common components of hazardous wastes on the characteristics of soils and standard clays. This study represents the first systematic effort to determine the effects of bulk organic solvents and solvent/water mixtures on the characteristics of clays. An attempt was also made to develop a model to predict the potential impact on groundwater quality that may result when a particular type of hazardous waste is disposed of onto a particular type of land or remolded clay barrier (liner).

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CONTENTS

Figures iv

Tables ix

Acknowledgement xi

1. Introduction 1

2. Summary and Conclusions 3

3. Recommendations 7

4. Literature Review 9

   Introduction 9

   Studies of Movement of Industrial Wastes to Groundwater 10

   Experimental On-Land Disposal Practices 12

   Sorption-Desorption and Ion Exchange 14

   Permeability of Soils 18

   Atterberg Limits 32

   Clay-Organic Studies: X-Ray Investigation of Swelling 33

   Octanol/Water Partition Coefficient 35

5. Methods 38

   Introduction 38

   Clay Mineralogy 38

   Particle Size Analysis 38

   Moisture Density Relationships 39

   Atterberg Limits 40

CONTENTS (continued)

Specific Gravity 41

Cation Exchange Capacity 41

Total Carbon and Carbonate Analysis 42

Swell Properties 42

Coefficient of Permeability for Liquids and Liquid Mixtures in Contact with Clays 43

X-Ray Diffraction Studies of Clays in Contact with Solvents and Solvent Mixtures 46

Determination of Major Ions 46

Determination of Sorption Isotherms for Volatile Organics 46

6. Results and Discussion 51

Introduction 51

Characteristics of Clays Used in This Investigation 51

Effects of Organic Solvents on Clay Lattice Spacing 61

Sorption Isotherm Studies 67

Swelling of Clays in Contact with Water, Organic Solvents, and Solvent Mixtures 81

Effects of Organic Solvents on Permeability . . . 106

Concluding Remarks 129

7. Survey of Current Practices for Land Disposal of Hazardous Wastes 134

Introduction 134

Summary of Responses 134

References 136

CONTENTS (continued)

Appendices

A. Data on Swell Properties of Clays A1

B. Data on Permeability of Clays to Organic Solvents B1

C. Summary of Responses of State Pollution Control Agencies to Requests for Information on Current Regulations and Practices for Land Disposal of Hazardous Wastes C1

D. Proposed EPA Hazardous Waste Guidelines D1

FIGURES

Number		Page
1	Constant-head permeameter	23
2	Falling-head permeameter	25
3	Effect of pumping on-line groundwater level . . .	27
4	Atterberg limits and indices	34
5	Pressure permeability column	44
6	Change in peak height (concentration) with time for benzene sorbed onto Ranger Shale	49
7	Moisture-density relationship for Kosse-Kaoline .	55
8	Moisture-density relationship for Ranger Shale .	55
9	Moisture-density relationship for Fire Clay . . .	55
10	Moisture-density relationship for Parker Soil . .	55
11	Freundlich isotherm for benzene sorption on Ranger Shale.	72
12	Freundlich isotherm for m-xylene sorption on Ranger Shale	72
13	Freundlich isotherm for carbon tetrachloride sorption on Ranger Shale	72
14	Freundlich isotherm for acetone sorption on Ranger Shale	72
15	Freundlich isotherm for benzene sorption on Kosse Kaoline	73
16	Freundlich isotherm for m-xylene sorption on Kosse Kaoline	73
17	Freundlich isotherm for carbon tetrachloride sorption on Kosse Kaoline	73

Figures (continued)

Number		Page
18	Freundlich isotherm for benzene sorption on Fire Clay	74
19	Freundlich isotherm for m-xylene sorption on Fire Clay	74
20	Freundlich isotherm for carbon tetrachloride sorption on Fire Clay	74
21	Chromatogram of m-xylene standard solution . . .	78
22	Chromatogram of m-xylene standard solution after 24-hr contact with Ranger Shale	78
23	Chromatogram of standard solution containing a mixture of xylenes	79
24	Chromatogram of standard solution of xylenes after three week exposure to Ranger Shale	79
25	Swell properties for Ranger Shale in benzene . .	82
26	Swell properties for Fire Clay in benzene	82
27	Swell properties for Ranger Shale in xylene . . .	82
28	Swell properties for Fire Clay in xylene	82
29	Swell properties for Kosse Kaoline in xylene . .	83
30	Swell properties for Ranger Shale in carbon tetrachloride	83
31	Swell properties for Kosse Kaoline in carbon tetrachloride	83
32	Swell properties for Fire Clay in carbon tetrachloride	83
33	Swell properties for Ranger Shale in trichloroethylene	85
34	Swell properties for Kosse Kaoline in trichloroethylene	85
35	Swell properties for Fire Clay in trichloroethylene	85

Figures (continued)

Number Page

36 Swell properties for Ranger Shale in acetone and in 50 volume percent acetone-water mixture . . 85

37 Swell properties for Kosse Kaoline 86

38 Swell properties for Fire Clay in acetone 86

39 Swell properties for Ranger Shale in deionized water 86

40 Swell properties for Ranger Shale in deionized water (duplicate) 86

41 Swell properties for Kosse Kaoline in deionized water 87

42 Swell properties for Fire Clay in deionized water 87

43 Swell properties for Ranger Shale in methanol . . 87

44 Swell properties for Ranger Shale in glycerol . . 87

45 Swell properties for Ranger Shale in mixture of acetone (25 mole %)and benzene (75 mole %) 88

46 Swell properties for Ranger Shale in mixture of acetone (50 mole %)and benzene (50 mole %) 88

47 Swell properties for Ranger Shale in mixture of acetone (75 mole %) and benzene (25 mole %) . . . 88

48 Swell properties for Ranger Shale in 50 volume percent mixture of xylene and deionized water . . 88

48a Comparison of swell properties of Fire Clay in CCl_4, acetone, and water: effects of low, intermediate, and high dielectric solvents 94

48b Comparison of swell properties for Kosse Kaoline in CCl_4, acetone, and water: effects of low, intermediate, and high dielectric solvents 95

48c Comparison of swell properties of Ranger Shale in CCl_4, acetone, and water: effects of low, intermediate, and high dielectric solvents 96

49 Relationship between solvent dielectric constant and percent swell of Ranger Shale 97

Figures (continued)

Number Page

50 Relationship between solvent dielectric constant and percent swell of Kosse Kaoline 98

51 Relationship between solvent dielectric constant and percent swell of Fire Clay 99

52 Coefficient of permeability of Ranger Shale to benzene 107

53 Coefficient of permeability of Ranger Shale to xylene 107

54 Coefficient of permeability of Ranger Shale to carbon tetrachloride 107

55 Coefficient of permeability of Ranger Shale to trichloroethylene 107

56 Coefficient of permeability of Ranger Shale to acetone 108

57 Coefficient of permeability of Ranger Shale to methanol 108

58 Coefficient of permeability of Ranger Shale to glycerol 108

59 Coefficient of permeability of Ranger Shale to deionized water 108

60 Coefficient of permeability of Kosse Kaoline to xylene 109

61 Coefficient of permeability of Kosse Kaoline to acetone 109

62 Coefficient of permeability of Kosse Kaoline to deionized water 109

63 Coefficient of permeability of Fire Clay to xylene 111

64 Coefficient of permeability of Fire Clay to acetone 111

65 Coefficient of permeability of Fire Clay to deionized water 111

Figures (continued)

Number		Page
66	Coefficient of permeability of Fire Clay to trichloroethylene	111
67	Coefficient of permeability of Ranger Shale to a mixture of acetone (75 mole%) and benzene (25 mole%)	112
68	Coefficient of permeability of Ranger Shale to a mixture of acetone (50 mole%) and benzene (50 mole%)	112
69	Coefficient of permeability of Ranger Shale to a mixture of acetone (25 mole%) and benzene (75 mole%)	112
70	Coefficient of permeability of Ranger Shale to a mixture of acetone (75 mole%) and carbon tetrachloride (25 mole%).	112
71	Representation of water-containing clay	116
72	Relationship between coefficient of permeability and octanol/water partition coefficient	118
73	Relationship between coefficient of permeability and dielectric constant for solvents in Ranger Shale	121
74	Relationship between coefficient of permeability and dielectric constant for solvents on Kosse Kaoline	122
75	Relationship between permeability and dielectric constant for solvents on Fire Clay	123
76	Coefficient of permeability as a function of packed bulk clay density	126
77	K vs. $\varepsilon^{0.75}/d^7$ for organic solvents and water on three clays	132

TABLES

Number		Page
1	Conditions for Organic Solvent Analysis	50
2	Particle Size Distribution	52
3	Clay Mineralogy	54
4	Optimum Moisture Contents	56
5	Atterberg Limits	56
6	Cation Exchange Capacity	58
6A	Exchangeable Na, K, Ca, and Mg	59
7	Major Ion Content of Clays Studied	60
8	Total Carbon and Carbonate Content	60
9	Results of X-Ray Diffraction Measurements of Air-Dried Ranger Shale after Exposure to Various Solvents	62
10	Results of X-Ray Diffraction Measurements for Air-Dried Kosse Kaoline in Contact with Various Solvents	63
11	Results of X-Ray Diffraction Measurements for Air-Dried Fire Clay in Contact with Various Solvents	64
12	Results of X-Ray Diffraction Measurements for Air-Dried Parker Soil in Contact with Various Solvents	65
13	Results of X-Ray Diffraction Measurements of Air-Dried Montmorillonite After Exposure to Various Solvent-Water Mixtures	66
14	d(001) Spacing for Clays in Contact with Pure Solvents	67
15	Sorption of Organic Solvents on Ranger Shale . .	69
16	Sorption of Organic Solvents on Kosse Kaoline . .	70

Tables (continued)

Number		Page
17	Sorption of Organic Solvents on Fire Clay	71
18	Freundlich Equation Constants for Sorption of Organic Solvents Onto Clays	75
19	Sorption of Organic Compounds Onto Clays At Equilibrium Concentrations of 1 mM	76
20	Percent Swell of Test Clays in Contact with Liquids Compared to Dielectric Constants and Dipole Moments of Liquid	93
21	Percent Swell of Clays Due To Hydrophobic Solvents In Relation To Organic Carbon Content of Clay . .	100
22	Classification of Clay-Organic Solvent Systems According to Swell Properties	101
23	Swell Properties of Ranger Shale in Five Solvent Mixtures	103
24	Equilibrium Permeabilities of Clays to Organic Solvents and Water	113
25	Density-Viscosity Ratios for Organic Solvents and Water	114
26	Permeabilities and Percent Swell for All Single Solvent Systems Tested	115
27	Permeabilities and Octanol/Water Partition Coefficients for Solvents on Three Clays	119
28	Clay-Soil Characteristics	125
29	Coefficients of Permeability for Four Binary Mixtures	127
30	Coefficients of Permeability for Typical Soils .	129
31	Calculated and Observed Permeability Values for Eleven Single Solvent Systems	133
A1 - A25	. . . .	A1-A27
B1 - B19	. . . .	B1-B23

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SECTION 1

INTRODUCTION

During the past several years, increasing emphasis has been placed on control of air and water pollution at the federal, state, and local levels. With stricter controls on air and water pollution and the increasing costs of associated pollution control equipment and fuel, interest in the land disposal of municipal and industrial wastes has increased. This, coupled with the essentially complete prohibition of ocean dumping has resulted in the on-land disposal of large amounts of processing-manufacturing chemical wastes. While land disposal of waste is often relatively easy and relatively inexpensive where inexpensive land is readily available, it is not without significant potential environmental problems, the most important of which is groundwater contamination.

Protection of the quality of groundwater resources of the US has been a grossly neglected area which needs immediate attention. Although the passage of the 1974 "Drinking Water Act" provides the legislation necessary to protect the US groundwater resources from contamination from wastes disposed of on land, in many cases the techniques and methodologies have not been available to properly implement or enforce these regulations. For example, this act makes provisions to prohibit on-land disposal of municipal and industrial waste where there is a significant potential for groundwater contamination. However, in order to properly implement this provision, procedures are needed which can be used to predict the transport of municipal and industrial waste components from their on-land disposal site to groundwaters. When developed, these tests should be employed routinely to provide the regulatory agencies and the individuals responsible for disposal of wastes, with "go" or "no go" information for a particular type of waste in a particular land disposal system.

Although wastes may contain one or more hazardous substances, whether they pose a threat of groundwater pollution or not will depend on a variety of factors including: quantity of waste, leachability, rainfall, permeability, attenuative properties of the soil, and the distance to and quality of the groundwater. In most cases, it is not known beforehand whether disposal of a given waste at a given on-land site will result in groundwater contamination. In fact, due to limited or non-existing groundwater monitoring, pollution incidents are not usually predicted, nor are they realized, until actual damage has been experienced.

To protect public health and the environment, it is desirable to develop a procedure or procedures that can be used for any given site to 1) evaluate the potential for groundwater degradation from potentially hazardous wastes, and 2) determine if a potentially harmful quantity of a waste is to be involved in a given disposal situation. These procedures should be incorporated into the standard site evaluation process used by regulatory agencies.

This research project was aimed toward development of procedures by which to evaluate the potential for groundwater contamination by hazardous industrial wastes disposed of on land. Studies were conducted to describe the attenuative properties of the soil, soil permeability, and the effects of a number of common components of hazardous wastes on the characteristics of soils and standard clays. This study represents the first systematic effort to determine the effects of bulk organic solvents and solvent/water mixtures on the characteristics of clays. An attempt was also made to develop a model to predict the potential impact on groundwater quality that may result when a particular type of hazardous waste is disposed of onto a particular type of land or remolded clay barrier (liner). It should be noted that while throughout this report, the clay-soils Kosse Kaoline, Fire Clay, and Ranger Shale are referred to as "clays," only portions of these materials were clay minerals.

SECTION 2

SUMMARY AND CONCLUSIONS

Increasing amounts of industrial wastes are being disposed of on land. This is a result of a variety of factors including increasingly stringent regulations to protect against air and water pollution. Land disposal of municipal and industrial waste carries with it a significant potential for groundwater contamination; there are numerous instances of groundwater pollution from such disposal operations. As part of this study, a review of state regulations governing land disposal has been conducted. It has been found that only a few of the 50 states have definitive regulations. Some states on the other hand, specify the maximum permeability of the subsoil strata in the disposal area, require the use of clay liners of a given thickness and permeability if the natural permeability is greater than the specified amount, and regulate the types of wastes that may be disposed of in these pits. Many of the states that specify a maximum permeability have not indicated how permeability tests should be conducted and in particular the types of liquids that should be used in the tests. It is generally recognized that there is need to develop a more technically valid approach for the control of land disposal of industrial wastes than exists today. Since many industrial waste disposal pits receive large amounts of organic solvents, it is conceivable that these solvents could be readily transported to groundwater.

The data obtained during this study have provided a basis for predicting the movement of hazardous organic chemicals through clays and soils. Models for the behavior of organic substances in dilute aqueous solutions in contact with clays, and for clays immersed in bulk liquids and liquid mixtures have been developed. These will aid pollution control agencies in assessing the potential environmental hazard associated with land disposal of industrial wastes. The specific conclusions reached are outlined below:

1. Sorption is an important parameter for assessing the attenuation of contaminants by clay liners and by soil and subsoil systems. Because of the large quantities involved in some industrial waste disposal operations, the organic solvents frequently used in manufacturing represent a significant potential for groundwater

contamination when disposed of on land. It is therefore important to examine the sorption of organic solvents on clays. Techniques have been developed during this study for obtaining valid sorption data for highly volatile organic compounds such as organic solvents. These techniques involve taking precautions to minimize the number of transfer steps, reducing the free volume above the liquid (head space) to a few cubic centimeters and preparing solution concentrations accurately using methods described in this report.

Based on the systems studied, sorption of hydrophobic solutes by the clays was extensive in most cases and showed a marked increase with compounds of increasing octanol/water partition coefficients. Of the three compounds tested with each of three clays, xylene (highest octanol/water partition coefficient of the three) consistently showed the greatest amount of sorption. Those clays richest in kaolinite tended to be the most effective sorbents.

It has been concluded that sorption by clays is an important mechanism by which the transport of low molecular weight organics from waste disposal pits to groundwater is minimized.

2. The shrink-swell properties of clays in contact with solvents is of importance in determining the ability of clay liners in industrial waste disposal pits to retain wastes. This study was the first systematic effort to examine the effects of bulk organic solvents and solvent mixtures on the swelling of clays. It can be concluded that swelling probably occurred through interparticle separation rather than through intercalation or complex formation. For a first approximation, the solvent dielectric constant gave an indication of the degree of swell of the clay with which it is in contact. The montmorillonite (expandable layer clay) content of the clay was of no consequence in predicting swell, but there was a correlation between percent clay swell and the percent organic carbon content of the clay.

   In some pure solvent systems, notably those having low dielectric constants, shrinking occurred probably due to dehydration of the clay by the solvent. That is, there was a transfer of water out of the clay with no commensurate replacement by solvent molecules.

   With respect to swell, each component of a solvent mixture appeared to have behaved independently of the others, so that swelling of clays was caused solely by that component having the greater (greatest) dielectric constant. In systems with a mixture of solvents, the degree of swelling of the clay will be roughly the same as it is in a system of the clay with the pure solvent of the greater (greatest) dielectric constant. Wastes containing solvents with only low dielectric constants should be mixed with a high dielectric solvent such as water during disposal in order to prevent cracking of clay liners. Additional work must be done on the effect of clay organic carbon content on the shrink-swell properties of a clay-solvent system in order to determine the significance of this parameter in influencing the ability of clay liners to retain industrial wastes.

3. The primary objective of this study was to determine the effect of organic solvents on the permeability of clay liners, soils, and subsoil systems to water-organic mixtures. An important contribution of this work has been the development of permeability test techniques for organic solvents. The conventionally-used techniques suitable for water are not satisfactory for use with many organic solvents because of the interaction between the sealants used and the solvent. The new procedure involved packing the clay directly into the column without the use of sealants.

   A somewhat surprising and important conclusion of this study was that the permeability of packed clay columns to organic solvents was less than to water. This can be attributed to the tendency of an organic molecule to escape from the aqueous, inter-aggregate phase and to thus be strongly sorbed on the clays, and to various other factors including microbial decomposition of the organic solvent and subsequent liberation of gases which clog clay pores. This biological interference was likely a factor in the permeability test results obtained for Ranger Shale.

   The correlation between the permeability of solvents through a clay, K, and their octanol/water partition coefficients, P, was such that the larger the value of P (greater escaping tendency from the aqueous phase), the lower the value of K. Also, there is an apparent relationship for a given clay between the solvent dielectric constant and the coefficient of permeability; the larger the dielectric constant, the greater the flow permeability. As expected, the coefficient of permeability is also markedly dependent upon the packed, bulk clay density; the denser the clay the lower the equilibrium permeability coefficient.

   The behavior of solvent mixtures in clay column tests was in general similar to the behavior of the most polar solvent component of the system, both in terms of the equilibrium values of K, and the variation of K with time.

During permeability tests with carbon tetrachloride, xylene, and benzene, breakthrough was observed. However, when benzene and CCl_4 were mixed individually with acetone, breakthrough was not observed over the 36-day test period. This phenomenon of breakthrough seemed to be related to the shrinking of the clays noted above. It is concluded that designed co-disposal of solvents may be an effective way of eliminating potential cracking of clay liners.

Based on the single solvent systems examined, the following empirical relationship has been derived for estimating the coefficient of permeability, K, (in cm/sec):

$$\log K = 1.17 (\log (\varepsilon^{0.75}/d^{7})) - 7.23$$

where ε = dielectric constant
d = packed bulk clay density (g/cc)

While most of the data obtained in this study fit this relationship, with further work it is likely that a more widely applicable relationship can be developed. An important conclusion of this study was, however, that the effect of organic solvents on the coefficient of permeability may be estimated from readily obtainable information, i.e., the dielectric constant of the solvent and the packed, bulk density of the clay.

4. Interlayer spacings as measured by X-ray diffraction were essentially constant for a given clay in contact with a variety of solvents and solvent-water mixtures. This indicates that in the presence of trace amounts of moisture, a characteristic clay-water complex is formed, and that there is no interlayer penetration of organic molecules under these conditions which alters the clay molecular structure.

From an overall point of view, this study has shown that organic solvents of the type that are commonly used in manufacturing can have a significant impact on the ability of disposal pit clay liners to retain industrial wastes. Further, information has been developed which will likely prove to be of significant value in providing guidance on the operation of industrial waste land disposal sites. It has been shown that simple solvent and clay properties can be used to predict their effects on transport of contaminants through packed clay disposal pit liners. There is a need for field studies to verify the conclusions drawn from this study.

SECTION 3

RECOMMENDATIONS

This study represented the first phase of a planned longer-term investigation designed to ascertain the potential for migration of organic solvents from industrial waste disposal pits to groundwater. The first phase of this study was to be devoted to pure solvent-defined clay systems in order to determine if any generalized relationships could be developed under controlled laboratory, simplified conditions. Based on these studies, the following recommendations have been made.

1. All liquid organic wastes should be tested prior to being disposed of on land, using the consolidometer, to determine whether they cause the specific clay of interest to shrink or swell. If shrinking is observed, as may be the case for low dielectric solvents, a spent solvent of higher dielectric constant or water should be added so that the mixture gives a smooth swelling profile. It is felt that frequency and extent of testing of this type can be significantly reduced once the general characteristics of the waste from a particular manufacturing process have been ascertained.

2. Using the relationship developed in this study an estimate should be made of the permeability coefficient of a waste material prior to disposal, to insure that the value of permeability is within the limits set by state regulations.

3. Because of the potential value of an equation which can be used to estimate permeability coefficients for a variety of diverse systems, further efforts should be directed toward establishing such a relationship, applicable to both pure solvents and to the most complicated mixtures. The direction that such an effort might take has been indicated in this study; but there is need for more laboratory data, particularly on mixtures, and for more sophisticated investigations to establish the mechanism of solvent movement through clay.

4. Additional column tests should be run using "sterilized" clays in order to avoid the complications which arise

from microbial activity. Using such a column a greater range and diversity of solvents and mixtures should be studied. Also, clays of different bulk densities and moisture contents should be tested in order to determine the effects of these parameters on permeability.

5. The apparent importance of clay shrinkage as it relates to shrinkage of clay liners used in waste disposal pits warrants that further work be carried out in this area in order that this phenomenon can be predicted given a knowledge of clay and solvent properties.

6. Field tests should be conducted, both with substances such as CCl_4, benzene, and xylene which show a tendency to migrate in bulk through clays, and with these substances mixed with acetone, mixtures which are well behaved in the laboratory. There is need to determine whether the conclusions reached in the laboratory phase of this study are equally valid under field conditions for a variety of natural substrates, clay liners, and waste mixtures.

SECTION 4

LITERATURE REVIEW*

INTRODUCTION

The groundwater supply of the United States is a major natural resource, which, until recently has been considered virtually immune to contamination by the activities of man. Yet during the past decade, numerous incidents of groundwater pollution from chemical spills and landfill seepage have been reported and have shown that even our sequestered reservoirs of potable water are vulnerable. The potential seriousness of the problem becomes apparent when it is realized that groundwater provides water for about 100 million people in the U.S. (Jeffrey, 1974), nearly half of the population.

Concern over the quality of the nation's groundwater is reflected in the clarity, specificity and stringency of recent legislation aimed at protecting this resource. The Safe Drinking Water Act of 1974 was the first major piece of water management legislation to specifically recognize groundwater as an indispensible segment of the total national water resource. This act was intended to protect underground sources of drinking water by regulating both deep-well injection of chemicals and on-land disposal of municipal and industrial wastes.

Concern for groundwater quality is further evidenced by the increased allotment of federal research funds for studying the movement and fate of hazardous chemicals in the aquatic and soil environments. One of the focal points of recently proposed federal regulations governing on-land disposal of municipal and industrial wastes, the December 18, 1978 Federal Register, is the protection of groundwater. In this section of this report, the results of these and related investigations which are pertinent to the present study are summarized.

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*Ted Palit co-authored drafts of parts of this section of this report

STUDIES OF MOVEMENT OF INDUSTRIAL WASTES TO GROUNDWATER

The variety of industrial chemicals that have been and may be disposed of or spilled on land is enormous and includes toxic heavy metals, mineral acids, volatile organic solvents, pesticides and highly refractory compounds such as PCBs. Members of all of these classes are potential threats to the quality of the nation's groundwater supplies. There have been several laboratory studies conducted to evaluate the potential for migration of industrial wastes through soil systems. For example, Houle _et al_. (1976) studied the migration potential of industrial wastes containing cadmium (from nickel-cadmium batteries, electroplating, water-based paint and inorganic pigment wastes) in laboratory test columns. The migration potential of cadmium was found to be largely dependent on the physical and chemical composition of the soil upon which the waste was placed. However, differences in waste composition and leachability caused large differences in migration of specific elements or compounds through the soil. Houle _et al_. (1976) also found that specific metals leach differently from waste mixtures, depending on the type of solid or solution complex in which the metal exists. The composition of the leachate and its solubilizing and exchanging characteristics determined how a specific metal migrated through a given soil.

Streng (1976) attempted to assess the impact of co-disposal of industrial hazardous waste materials containing Hg, Cr, Cu, Zn, Pb, etc. with municipal solid waste. In general, there was a reduction in the moisture adsorption capacity resulting from the combining of the municipal solid waste with semi-solid industrial wastes containing high concentrations of heavy metal contaminants. Metallic ions became more soluble due to acid and reducing conditions. Mercury was converted either chemically or microbially, to a form more amenable to transport. Municipal solid waste and refinery sludge mixtures underwent rapid decomposition which reduced the quantity of organic matter in the leachate.

The transport of the chelating agent NTA to groundwater under various conditions was studied by Dunlap _et al_. (1971). They concluded that when NTA moves through unsaturated soil, rapid and complete degradation to inorganic nitrogen compounds and carbonate results. However, if NTA is transported through saturated soil, degradation is quite limited and a major portion of the compound reaches the groundwater intact. Under these circumstances, higher concentrations of complexed metals such as iron, zinc, chromium, lead, cadmium, and mercury, would be likely to be transported to the groundwater.

Walker (1973) investigated several hazardous material disposal sites for their potential for transmitting contaminants to groundwater. He found that contaminants from disposal sites may move through aquifers in a bulb-like mass at rates of a few feet per year. Therefore, a fairly small quantity of a toxic substance may enter a well as a hazardous slug several years after it has been deposited on land.

Pettyjohn (1974) examined groundwater pollution problems from the disposal of neutralized pickling liquors (wastes) into an abandoned strip mine in eastern Ohio. He monitored all of the surrounding and nearby waterbodies and found that water quality was adversely affected by polluted groundwater drainage from the disposal area. The samples collected from disposal pit seepage were characterized by low pH and high concentrations of dissolved solids, hardness, sulfate, chloride, nitrate, iron, fluoride, aluminum, chromium, nickel and zinc. In addition to contamination from the disposed industrial waste, acid mine drainage from surrounding areas was found to degrade both surface and groundwater quality. It was concluded that the problem of acid mine drainage would not have occurred in the abandoned strip mine had the mine not been used for waste disposal.

Two landfills, one 27 years old and the other 41 years old, in the upper glacial aquifer on Long Island, New York were studied by Kimmel and Bairds (1974). The plumes of leacheate from these landfills were found to sink to the bottom of the aquifer and extend out about 3,200 and 1,500 m, respectively. The pH in most of the leacheate-contaminated groundwater ranged from about 7 near the landfills to about 5 near the perimeter of the plume. Heavy metals other than iron, manganese, and zinc were not found in concentrations greater than several tens of micrograms per liter in the plume. The authors concluded that lining the landfill and collecting the leacheate to eliminate a potentially dangerous source of contamination, may be worth the added cost.

Groundwater pollution problems caused by a leaking gasoline pipeline near the City of Los Angeles were the subject of a paper by Williams and Wilder (1971). It was estimated that 250,000 gallons (950 m^3) of gasoline had seeped into the groundwater, polluting the groundwater supply of the area. Skimming operations to drain off gasoline resulted in recovery of 50,000 gallons (190 m^3). The area has been closely monitored since these remedial measures were taken. Most of the wells in the area now have only a taste or odor of gasoline with two of the wells showing detectable levels of free gasoline. It is hoped that bacteria will eventually break down the residual chemicals so that the aquifer may be restored to service.

In this connection, Golwer et al. (1971) investigated the process of self-purification of groundwater near disposal sites. The results of the study indicated that many pollutants are, in fact, eliminated by geochemical and biochemical processes in groundwater. Organic compounds such as gasoline residue may be decomposed by bacteria.

Osgood (1974) reviewed the literature on over 200 on-land spills of petroleum and petroleum products and concluded that regardless of volume discharged, all were potentially dangerous. The critical factor in determining the fate of the material, according to him, was the hydrogeologic character of the area, particularly the direction of groundwater flow.

A specific incident involving spillage of a petroleum product was reported and studied in detail by Delfino and Dube (1976). They monitored nine domestic and industrial wells in the vicinity of an accidental phenol spill and found that groundwater in the area (up to 400 m from the affected site) contained measurable concentrations of the compound during the 19-month study period. During this time there was also an increase in the incidence of gastrointestinal disorders and mouth sores of the people using this water for drinking. The temporal and spatial clustering of these symptoms strongly suggested that an epidemiological episode related to the phenol spill had occurred.

Lewallen (1971) investigated a farm well which was polluted with pesticides derived from contaminated soil placed near the well casing. Water and soil in and around the well were monitored for more than four years and it was found that both DDT and toxaphene persisted over this period. Levels in the sediment were much higher than those in the water, probably because of the low aqueous solubility of these substances and their tendency to sorb onto clays. Vertical soil sampling in the area indicated that the pesticides had moved down ground water only slightly.

Gibb (1976) evaluated the extent of groundwater pollution from surficial toxic waste disposal sites in humid regions. He found coring to be an effective tool for mapping the migration patterns of chemical pollutants. He also provided field data to verify the effectiveness of various types of soil to adsorb or retain different chemical pollutants.

EXPERIMENTAL ON-LAND DISPOSAL PRACTICES

Land disposal of industrial and hazardous wastes has been commonly practiced all over the U.S. In most cases the potential impact of such operations on groundwater quality was not investigated. It is only recently that the need for selectivity in siting, and strict control of disposal practices has become recognized. As discussed below, a variety of factors is involved in deciding where and with what precautions a particular waste should be disposed.

Snyder et al. (1976) studied the land disposal of oil refinery wastes and evaluated methods of applying and treating these. The investigation was conducted in a semi-arid area and supplemental fertilizer was applied. Adequate drainage control, soil characteristics which allow good drainage, and microbial activity were the major factors considered during site selection. Soil samples were taken from established land plots and analyzed to determine soil characteristics, nutrient levels, heavy metals, pH, oil content, dehydrogenase activity, soil respiration, microbial activity, and microbial composition and density. The chemical analysis of the soil showed that the heavy metal content did not change over this one-year study period. The pH values also did not change appreciably. On fertilized plots, oil degradation was found to be about 80 percent complete within one year. On a study plot that had not been fertilized, the oil had degraded only 55 percent.

Wiles and Lubowitz (1976) explored the possibility of disposing some solid or semi-solid hazardous industrial wastes containing arsenic, lead, mercury, selenium, beryllium, cadmium, zinc and chromium by encapsulating them with a plastic jacket. They first used a binder resin to agglomerate the waste and then encapsulated it with a 0.25 inch (0.64 cm) thick jacket of high density polyethylene and fused it with powdered polyethylene, in situ. The test specimens were subjected to leaching with simulated ocean water for 120 days. The leaching data indicated that the system had great ability to prevent or at least limit pollution by leaching to acceptable levels. The specimens were also tested for other properties such as compressive strength, freeze-thaw resistance, impact strengths, puncturability, etc. The overall performance of the specimens was found to be highly satisfactory. The investigators therefore recommended that the polymeric encapsulation process be used for disposal of hazardous wastes containing constituents such as sodium meta-arsenate and arsenic trisulfide, etc., which may not be adequately manageable by other techniques.

The effect of different clay liners in attenuating selected trace elements such as As, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn from landfill leachate was discussed by Fuller (1977). They observed different migration rates of various trace elements through soils and found that organic constituents in the waste had an effect on Hg attenuation. The kinds of clay materials they recommended for liners were: agricultural limestone, hydrous oxides of iron (ferrous sulfate mine waste), lime-sulfur oxide (stack-gas waste), certain organic wastes and soil sealants (natural clay material).

Liskowitz et al. (1976) examined the efficacy of ten natural and synthetic materials (bottom ash, fly ash, vermiculite, illite, Ottawa sand, activated carbon, kaolinite, natural zeolites, activated alumina, and cullite) for removal of contaminants in the leachate and liquid portion of three different industrial sludges, by sorption. They found no single sorbent of those examined that could significantly reduce the concentration of all the contaminants in a leachate to acceptable levels. They did find, however, that depending upon the type of sludge disposed, a combination of sorbents can be used to reduce the contaminants in the leachate to acceptable levels.

SORPTION-DESORPTION AND ION EXCHANGE

Among the most important soil properties influencing the ability of a soil to retard the movement of hazardous chemicals are sorption-desorption and ion exchange. Considerable effort has been expended to understand these complex processes and while there appears to be much literature dealing with the uptake of metals and polar organic molecules by clays, there has been very little written on the sorptive behavior of volatile, weakly polar organics. This review focuses on the interactions of organics with clays.

Sanks et al. (1975) investigated cation exchange capacity (CEC) and carbonate content of different clay materials with respect to their clay mineralogy. Their data showed that CEC of clays increased both with increasing percent montmorillonite and decreasing percent carbonate. Also, if two clays with the same percent montmorillonite were evaluated for CEC, the one with the lower percent carbonate would exhibit the highest CEC. They concluded that the decreasing values for CEC resulting from increasing percent carbonate may be due in part to the calcium carbonate fraction exchanging Ca^{++} with the clay mineral fraction.

McAfee (1959) studied the replacement of inorganic cations on montmorillonite by base exchange with organic compounds. Replacement of sodium from the homoionic Na-bentonite and the replacement of divalent Ca^{++} and Mg^{++} from Ca-Mg bentonite were studied for comparison. The results of the experiments showed that sodium is replaced relatively easily by the large organic cation on the Na-bentonite compared with Ca^{++} and Mg^{++} replacement on Ca-Mg bentonite.

Adsorption of anionic, cationic and nonionic surfactants onto montmorillonitic soils and kaolinite was the subject of an investigation by Law and Kunze (1966). They observed that anionic surfactants were not appreciably adsorbed and that anion exchange capacity of the kaolinite appeared to be equal to or somewhat greater than that of montmorillonite. Cationic surfactants were strongly adsorbed to all the clay samples in amounts either equal to or greater than the cation exchange capacity of the soils. The excess, it was speculated, was held by Van der Waals forces between the alkyl radicals. Montmorillonitic clays adsorbed considerably greater amounts of nonionic surfactants than kaolinite. The amount of adsorption by the clays was highly dependent on the surfactant concentration.

A radiochemical-tracer technique was used by Wayman et al. (1963) to study the adsorption of ABS (alkylbenzenesulfonate) on montmorillonite. They found that the adsorption of ABS on montmorillonite depended on the length of the alkyl chain and on pH. Montmorillonite clay adsorbed more pentadecyl ABS per gram than dodecyl ABS and more ABS from acid or neutral solutions than from alkaline solutions. For ABS adsorption, they found the optimum condition to be pH 4.

Aly and Faust (1964) examined the uptake of the herbicide 2,4-D and its ester derivatives on kaolinite, Wyoming bentonite (a montmorillonite clay), and Fithian illite. Results were analyzed using the Freundlich equation and it was found that sorption of these hydrogen bonding compounds from aqueous solution was insignificant (0.02 to 0.14 mg/g).

Huang (1971) looked at a variety of factors of possible significance in the sorption behavior of pesticides in aquatic systems. In the pH range of 6 to 10, decreasing the pH had the effect of slightly increasing the sorption of dieldrin on montmorillonite, whereas varying the temperature (between 10° and 30°C) caused no appreciable change in this system. Likewise, addition of salt, various organic pollutants such as glucose and alanine, and soluble organic matter from domestic wastewater had little or no effect on dieldrin uptake by montmorillonite.

Huggenberger et al. (1973) discussed adsorption and mobility of pesticides in soils and noted that pesticide molecules in general are strongly adsorbed by soils having high organic content and/or high clay content, but only weakly adsorbed by sandy soils. The latter observation is consistent with an earlier study by Boucher and Lee (1972) who found that lindane was sorbed to only a small extent by natural aquifer sand. Boucher and Lee also found that dieldrin was taken up in greater quantity than lindane in this sand system. As a rule, pesticides with a low water solubility are sorbed to a greater degree than those with higher aqueous solubility.

Hoffman and Brindley (1960) investigated the sorption of nonionic aliphatic molecules from aqueous solutions onto montmorillonite. It was concluded that a chain length of from five to six units is necessary for these molecules to show any appreciable sorption. For larger molecules (up to 10 units) the effect of increased chain length is to increase sorption. Also important is the electron withdrawing capacity of the functional group attached to the hydrocarbon chain. Molecules with stronger electron withdrawing groups, it was found, tended to be sorbed to a greater extent.

As part of their effort to determine the suitability of clay beds for storing industrial wastes, Sanks _et al_. (1975) studied the sorption of acetone, acetaldehyde and phenol onto five Texas clays. Sorption at an equilibrium concentration of 0.1 moles/liter, ranged from 1 to 90 mmoles/kg of clay, with acetaldehyde showing greater uptake than either phenol or acetone.

The only reported attempt to measure sorption of highly volatile organics from dilute aqueous solutions was discussed by Sanks _et al_. (1975) who remarked on the extreme experimental difficulties encountered in working with benzene. Because of errors associated with the transfer, centrifugation and analysis of aqueous benzene solutions, no data were published.

Lee and Jones (1978) have recently reviewed the state-of-the-art in assessing the significance of sorption-desorption for predicting the environmental chemistry-fate of organic contaminants. While their review was primarily directed toward dilute, aqueous slurry systems such as might be associated with suspended sediments in surface waters, it contains some information that may be useful in assessing the significance of sorption in groundwater systems. The following section has been extracted from their review.

Considerable progress has been made in the past few years in developing techniques for assessing the extent that sorption reactions may occur for contaminants in the aquatic environments. From relatively simple laboratory batch-type sorption experiments, it is now possible to derive information that can be used to predict, in a general way, whether sorption-desorption processes will likely be of major significance in influencing the environmental chemistry-fate of a chemical contaminant in aquatic environments.

To a large extent, environmentally relevant sorption research has been restricted to pesticide-soil systems (Karickhoff - US EPA, Athens, GA, personal communication). According to Karickhoff, for these types of systems, the extent of sorption has been related to pesticide properties (such as pK_a, pK_b, water solubility, and polarity) and soil properties (such as particle size distribution, organic matter content, and cation exchange capacity (CEC)).

The Freundlich equation,

$$x/m = KC_e^{1/n} \quad (1)$$

is frequently used to describe the adsorption equilibrium, where x/m is the mass of contaminant sorbed per unit mass of adsorbant, C_e is the equilibrium solution concentration, and K and n are constants. Some investigators choose to use this for environmental chemistry-fate modeling. Deviation of the value of n from 1, a common observation (AIBS, 1974), reflects the non-linearity of the process. If n were 1, then K would equal the partition coefficient, K_p defined in Equation 2. According to Karickhoff (personal communication), sorption of many organic compounds on sediment and suspended particulates in dilute aqueous systems is approximately linear and can be described in terms of the linear partition coefficient. This has been described by Baughman and Lassiter (1978) by the equation:

$$K_p = [P]_A/[P] \quad (2)$$

where K_p is the partition coefficient, and $[P]_A$ and [P] are equilibrium concentrations of the contaminant on the sorbent and water, respectively.

One of the most important factors affecting the partitioning of many organic contaminants between sediment and water is the organic carbon content of the sediment. It has been found that it is frequently useful to normalize sorption partition coefficients by the organic carbon content of the sediment or soil. An adsorption constant (K_{oc}) is defined as the amount of chemical adsorbed per unit of organic carbon (in ppm) divided by the concentration of the chemical dissolved in the water (in ppm). While this normalization has been found to be applicable to a large number of organic compounds especially non-ionics, it is not applicable to some of the other groups of organic compounds. Further work is needed to define the major factors controlling the sorption-desorption of these compounds in natural water sediments.

During the past several years, the US EPA Athens, GA, laboratory has undertaken a substantial research effort devoted to environmental chemistry-fate modeling. A significant part of this effort has been devoted to sorption-desorption of contaminants on natural water particulate matter and soils. Some of this work has been published (e.g., Baughman and Lassiter, 1978). Substantial parts of the results of this effort are in preparation as reports and papers or are in press at this time. The reader is referred to publications of this group as well as the review paper by Hamaker (1972) for further information on the state-of-the-art of modeling sorption-desorption processes in natural water systems and soils. The work conducted by this laboratory's staff and their contractors (e.g., Baughman and Lassiter, 1978; Karickhoff et al., 1979) as well as others has resulted in the following general conclusions:

1. The sorption of contaminants occurs to about the same extent on sediments and soils.
2. When normalized by sediment organic carbon content, the sorption of neutral organic compounds on sediments from different areas varies by a factor of 2 to 3 (Baughman and Lassiter, 1978). This is an extremely important conclusion which, if substantiated based on additional studies, greatly simplifies the prediction of the environmental behavior of many organics that tend to sorb, since the results of sorption tests conducted on one or a few sediments would in general be applicable to natural water systems located throughout the world.
3. While much of the sorption on natural water particulate matter is rapid (essentially complete within a few hours) and reversible, there are some compounds which apparently do not desorb or do so very slowly.
4. In general sorption on natural water particulate matter has a low temperature coefficient (activation energy).
5. One of the most promising recent developments is the correlation between the distribution coefficient for the uptake of dilute neutral organics by natural water solids and the octanol/water partition coefficient. A relationship of this type is to be expected for a large group of organic chemicals, especially the non-ionic type. Results of studies at the US EPA-Athens, GA laboratory provide the information needed to estimate sorption distribution coefficients from octanol/water partition coefficients (Karickhoff et al., 1979). Also Kenaga and Goring (1978) have recently completed a review of this topic.

PERMEABILITY OF SOILS

Permeability is the ability of a material to transmit water or other fluids. A material is said to be permeable if it contains continuous voids. Since such voids are contained in all soils including the stiffest clay, and all non-metallic construction materials including sound granite and neat cement, all of these materials show some degree of permeability. Furthermore, the flow of water through all void-containing solids obeys the same general laws.

Soil permeability is one of the most important soil characteristics in the study of subsurface pollution problems since migration of the pollutant itself is likely to be dependent on the permeability of soil. In the design of a confinement area for hazardous chemical disposal, permeability characteristics of the liner and strata in the disposal area should be determined in order to prevent pollution of groundwater by chemical contaminants. The permeability tests should be run with individual potential contaminants or mixtures of potential contaminants rather than with water only. Presented below is a summary of the current general knowledge related to permeability of both soils and subsoil systems as it relates to the movement of hazardous materials.

Coefficient of Permeability

Taylor (1948) discussed in detail the flow of water through the pores of soil. The pores of most soils are sufficiently small so that flow of water through them is laminar. In laminar flow, the water flows along definite paths which never intersect other flow paths. However, in coarse soils, the flow may sometimes be turbulent where the flow paths are irregular and twisting, crossing and recrossing at random.

Darcy (1856) demonstrated that the rate of flow of water through porous media is proportional to the hydraulic gradient. According to Darcy's Law,

$$\nu \propto i \qquad (3)$$

where ν = velocity of flow (m/sec)
i = hydraulic gradient (m/m)

$$\nu = Q/A \qquad (4)$$

where Q = flow through the aquifer per unit time
A = cross-sectional area of the aquifer

From Equations (3) and (4)

$$Q \propto Ai$$

$$Q = KAi$$

$$\therefore Q = KA\ (\Delta h/\Delta L) \qquad (5)$$

where K = coefficient of permeability

$\Delta h/\Delta L$ = hydraulic gradient

The coefficient of permeability, K, has the units of velocity. It can be interpreted as the velocity of flow under unit hydraulic gradient.

Permeability, Hydraulic Conductivity and Transmissibility

There is considerable variation in the definition of the terms permeability, hydraulic conductivity, and transmissibility by different authors and investigators. Walton (1970) and Black (1965) defined hydraulic conductivity (K) in the same way as the coefficient of permeability has been defined, i.e., the velocity of flow under unit hydraulic gradient. They have, however, defined permeability as a function of hydraulic conductivity, as follows:

$$P = K\eta/\rho g \qquad (6)$$

where K = hydraulic conductivity
P = permeability
η = fluid viscosity
ρ = fluid density
g = acceleration due to gravity

Thus, according to these authors, hydraulic conductivity has the units of velocity while permeability has the units of length squared.

Walton (1970) defined transmissivity as follows:

$$T = KD \qquad (7)$$

where T = transmissivity
K = hydraulic conductivity
D = depth of aquifer

Transmissivity is thus defined as the rate of flow of water through a vertical strip of the aquifer of unit width, extending through the total thickness of the aquifer under unit hydraulic gradient.

From an overall point of view, the literature seems to indicate that authors and investigators with geoscience backgrounds prefer the term "hydraulic conductivity" and very seldom use the term "coefficient of permeability". The National Water Well Association (NWWA) usually uses the term hydraulic conductivity in most of their publications. But, Hallberg and Martinell (1976) used the term permeability in one of the recent publications of NWWA. Todd (1959) defines both of these terms, coefficient of permeability and hydraulic conductivity, as being analogous. Walton (1970) also refers to the terms as being analogous, but confused them in later applications with permeability. While in general no strict principle has been followed in any area for the use of these terms in this study, coefficient of permeability and hydraulic conductivity are considered to be analogous terms; but, permeability is ideally considered to be a property of the porous medium alone.

Measurement of Coefficient of Permeability

The coefficient of permeability is one of the most important characteristics of clay material to be considered in assessing the suitability of the material for use as liners in hazardous waste disposal sites. Coefficients of permeability are determined under the assumption that Darcy's Law is applicable. The fundamental assumption in the application of Darcy's Law is that flow in a porous medium is laminar. The Reynold's number (N_R) has been developed as a criterion to distinguish between laminar and turbulent flow, and is expressed as:

$$N_R = \rho v D/\eta \tag{8}$$

ρ = density of fluid
v = velocity
D = diameter of the fluid path
η = viscosity of the fluid

To adapt this criterion to flow in a porous medium, the apparent velocity defined by Darcy's Law is used for v and an average grain diameter, d, is substituted for D in the equation for Reynold's number. According to Todd (1959), when various investigators have attempted to estimate the value of Reynold's number to determine the condition of flow in groundwater, they have found the value of Reynold's number to vary widely in the range of 60 to 700, below which laminar flow could be possible and above which the flow condition could be termed turbulent. This implies that the Reynold's number is not a good criterion for judging the condition of laminar or turbulent flow in groundwater. For almost all natural groundwater movement, however, $N_R < 1$ and Darcy's Law should be applicable. Moreover, materials with low coefficients of permeability (silt, clay, etc.) have

N_R values much less than one. Burmister (1954) presented the realm of validity of Darcy's Law and showed that in all materials finer than silt, flow will always be laminar.

The coefficient of permeability can be determined in three ways:

1. By laboratory tests on soil samples.

2. By field tests.

3. By use of empirical formulae.

Each of these approaches is discussed below.

Laboratory Determination--

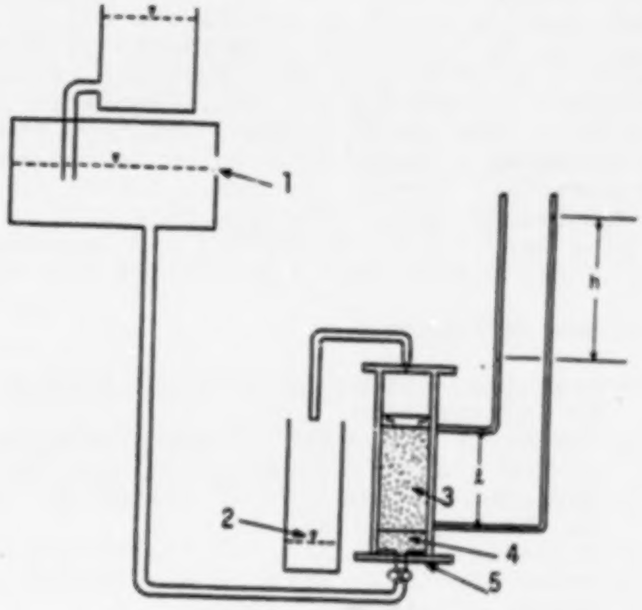
The most convenient and moderately reliable way to determine the coefficient of permeability is by laboratory tests on soil samples. It is based on the measurement of the quantity of water that flows under a given gradient through a soil sample of known length and cross-sectional area in a given period of time. Terzaghi and Peck (1948) were the original investigators of the characterization of soil permeabilities and different methods of laboratory analysis. Kezdi (1974) and Black (1965) also presented detailed procedures to determine the coefficient of permeability. As discussed by them, laboratory determination of coefficients of permeability can be made by two methods.

1. Constant-head permeability test.

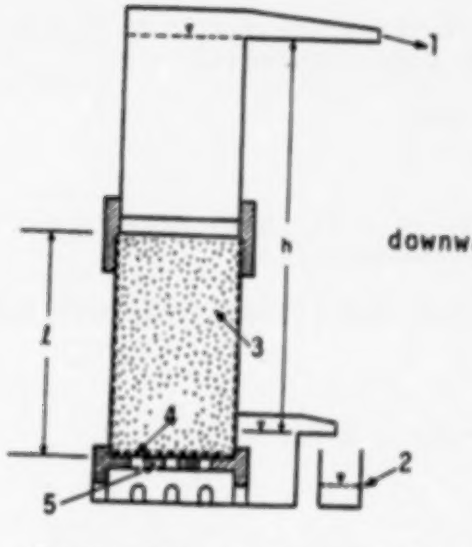
2. Falling-head permeability test.

Constant-head permeameters are particularly suitable for testing highly pervious, coarse-grained soils. For soils with medium to low permeability, the falling-head permeameters are used.

The principle of the constant-head permeameter is shown with sketches in Figure 1. Upward and downward flow types can be constructed. In both, water levels are kept constant by means of overflows. The hydraulic gradient, i, can be computed as the difference between the constant water levels, h, divided by the depth of the sample, ℓ. Operation of both the upward-flow and downward-flow constant-head permeameters depends on the ability to obtain a measurable quantity of leachate. The upward-flow type with piezometer tubes is more applicable for samples with less pervious, fine sands and silty sands. More reliable results can be obtained by measuring the actual water pressure in the sample by means of piezometer tubes. The discharge, Q, during a given time, t, is collected in a graduated cylinder to determine the volume discharged.



upward flow type



downward flow type

Figure 1. Constant-head Permeameter

1 - overflows; 2 - measuring cylinder; 3 - soil sample;
4 - screen and filter layer; 5 - base plate
(See text for explanation of symbols)

For soils of low permeability, measurable flow through a sample cannot easily be obtained by the constant-head test. Moreover, test results would be unreliable due to evaporation. In such cases, the falling-head permeameter is more suitable. Figure 2 displays in principle the operation of such a permeameter. A cylinder containing the soil sample is placed into a base fitted with a fine gauze screen. On top, the cylinder is plugged with a rubber stopper into which is inserted a graduated standpipe or burette. During the test, the fluid level in the pipe will continuously drop. The quantity of fluid that flowed through the pipe need not be collected and measured in this test, since it can be calculated from the fall of the fluid level.

If, as shown in Figure 2,

h_1 = height of the water in the standpipe from trough at initial time, t_1
h_2 = height of the water in the standpipe from trough at the end of the period of observation, t_2
h = difference of height of the water column $(h_1 - h_2)$ in the intermediate time, t
a = cross-sectional area of the standpipe
A = cross-sectional area of the sample
ℓ = length of the soil sample

then, the velocity of flow in the standpipe $= -(dh/dt)$ (9)

(- is used to indicate that the water level decreases as time increases)

According to Darcy's Law

$$Q = A\ (h/\ell) \tag{10}$$

or $Q = -a\ (dh/dt) = KA\ (h/\ell)$ where K is the coefficient of permeability.

Separating the variables and integrating both sides, within the limits,

$$-a \int_{h_1}^{h_2} (dh/h) = K\ (A/\ell) \int_{t_1}^{t_2} dt \tag{11}$$

$$\text{Hence } K = (a\ell/A) \cdot \{1/(t_2 - t_1)\} \ell n\ (h_1/h_2) \tag{12}$$

Sanks et al. (1975) attempted to conduct laboratory permeability tests with both undisturbed and remolded samples. Their experiments with undisturbed samples proved unsuccessful.

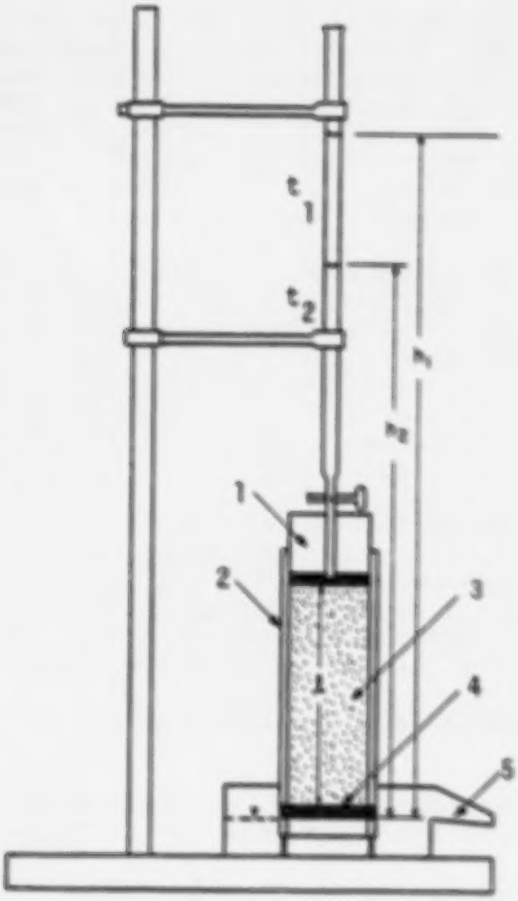

t1
t2
h1
h2
1
2
3
4
5
L
x

Figure 2. Falling-head Permeameter

1 - stopper; 2 - cylindrical column; 3 - soil sample;
4 - screen and filter; 5 - overflow
(See text for explanation of symbols)

Further, they encountered lack of reproducibility of results in their studies with remolded samples. They concluded that laboratory permeability tests on cores collected in the field, even from closely spaced test borings in the same horizon, can produce results which vary by factors of five or more.

Field Measurement. "K" values obtained from laboratory tests often differ considerably from the true coefficients of permeability of the soil obtained by field measurements. There are many reasons for this discrepancy, the most important being that the permeability of natural soil masses is greatly influenced by the heterogeneity and delicate, or even undetectable, stratification of the soil and by the uneven distribution of the fine-grained fractions within it. Such effects can rarely be simulated in normal laboratory testing.

A simple approach to determination of field coefficients of permeability has been described by Black (1965). This method, the Auger-Hole method, involves construction of a cavity with a minimum of soil disturbance. Flow of water into the soil or out of the soil into the cavity is then measured, depending on whether the position of the cavity is above or below the water table. Coefficient of permeability can be determined by direct substitution into Darcy's equation.

A more sophisticated method for the field determination of coefficients of permeability is the pumping test. To conduct a pumping test it is necessary that the well yield be in a steady state. Figure 3 shows a section through a well and surrounding aquifer. In order to determine permeability of the aquifer in the region of the well, the following assumptions are made:

1. The water table is of infinite extent in the horizontal direction.

2. The water bearing stratum is homogeneous, horizontal and is of constant thickness.

3. The test well is a perfect well. This means that it extends to the bottom of the permeable stratum and is perforated over the section which is below the water table.

4. In its original state, the groundwater is at rest and there is no flow into or out of the system during the test.

Pumping generates a radial flow of water forward to the center of the well and as a result the water table assumes a curved surface called the draw-down surface. If the pumping is continued for a sufficient time, a steady-state flow is eventually attained.

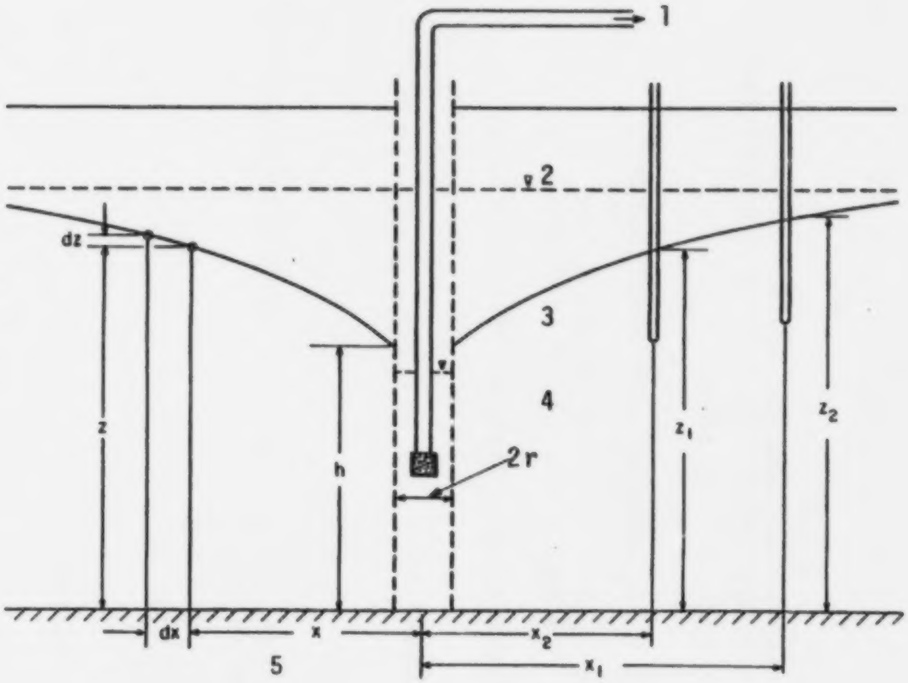

1
2
3
4
5
2r
dz
z
h
dx
x
x_2
x_1
z_1
z_2

Figure 3. Effect of pumping on-line groundwater level

1 - To pump; 2 - original groundwater table; 3 - lower groundwater surface; 4 - permeable layer; 5 - impervious layer

(See text for explanation of symbols)

For computation of the coefficient of permeability, Darcy's Law is applicable at the steady-state condition. The rate of radial flow through a cylindrical surface of radius r is proportional to the cross-sectional area of the aquifer multiplied by the hydraulic gradient.

$$q \propto A_\gamma \, i \tag{13}$$

where q = flow through the well
A_γ = cross-sectional area of the aquifer
i = hydraulic gradient

Therefore $q = KA_\gamma \, i = KA_\gamma \, (dz/dx) = K \, 2\Pi xz \, (dz/dx)$ (14)

where K = coefficient of permeability
(z and x are shown in Figure 3)

Separating the variables and integrating both sides,

$$\int ZdZ = \int (qdx/2K\Pi x)$$

$$Z^2 = (q/\Pi K) \ln x + c \tag{15}$$

The constant of integration, c, can be determined from the boundary conditions as follows:

when $x = r$, $Z = h$

$$C = h^2 - (q/\Pi K) \ln r \tag{16}$$

Substituting C,

$$Z^2 - h^2 = (q/\Pi K)\,(\log_e - \log_e r)$$

Solving for K,

$$K = (q/\Pi) \, \{\ln (x/r)\} \; /(Z^2 - h^2) \tag{17}$$

The derivation is based on several simplifying assumptions. The highest deviation from the theoretical assumptions exists in the immediate vicinity of the test well. Therefore, instead of using the above equation for a single well, it is advisable to make two observation wells located at some larger distances x_1 and x_2 and use the heights Z_1 and Z_2 to determine the coefficient "K." The formula thus becomes:

$$K = (q/\Pi)\ \{\ell n(x_1/x_2)\}\ /(Z_1^2 - Z_2^2) \qquad (18)$$

Naney et al. (1976) studied hydraulic conductivity of aquifers and attempted to formulate predictive models for the evaluation of groundwater paths. They used two approaches in the study. One was the parallel steamtubes concept and the other was the converging steamtube concept with flow converging toward the center. The latter provided a hydraulic conductivity distribution more nearly like that expected.

Although the pumping test is the best approach by which to determine the value of the true coefficient of permeability in the field, it cannot be used to determine "K" values for materials such as silt and clay. First, with clay of low permeability, it is not possible to obtain a steady state condition of pumping. Second, the above list of assumptions is not applicable for any type of clay material. Therefore, for fine-grained soils with very low coefficients of permeability, there are very few reliable field methods for the determination of "K" values.

Use of Empirical Formulae. The determination of coefficients of permeability by the use of empirical formulae is based on Poiseuille's Law which expresses the relationship governing the flow of water through round capillary tubes. The law says that the average velocity through a capillary tube is proportional to the square of the diameter of the tube. Therefore, it is reasonable to expect that the seepage velocity through a given soil and the coefficient of permeability of the soil are proportional to the square of the average pore dimensions. Since grain size has the greatest effect on the size of the pore, it may be concluded that the coefficient of permeability is proportional to the square of the grain size.

Hazen (1911) found that the permeability of filter sands could be roughly expressed by

$$K = 100\ (D_{10})^2 \qquad (19)$$

where D_{10} is the grain size diameter, such that the aggregate weight of all smaller size grains is 10 percent of the total weight of the sample. This is also called the effective size or Hazen's Effective Size. Hazen's observations were made on sands for which the effective sizes were between 0.1 and 3 mm diameter and for which the uniformity coefficient (the ratio of D_{60} to D_{10}) did not exceed 5.

Porosity and void ratios are also measures of pore spaces in a soil sample. They are defined as:

$$\text{Porosity} = e/(1+e) \tag{20}$$

where e = void ratio

$$e = V_v/(V-V_v) \tag{21}$$

V = total volume
V_v = total volume of voids

Terzaghi and Peck (1948) developed a formula for fairly uniform sands, which reflects the effects of grain size and void ratio:

$$K = 200\ (D_{10})^2\ e^2 \tag{22}$$

where D_{10} = effective grain size
e = void ratio

Amer and Awad (1974) studied the dependence of the hydraulic conductivity on the uniformity coefficient, effective diameter and the void ratio for cohesionless (natural sand and gravelly sand soils) soils. They developed an empirical formula for the determination of coefficients of permeability for cohesionless soil as follows:

$$K = 3.5 \times 10^{-4}\ \{e^3/(1+e)\}\ U^{0.6}\ D_{10}^{2.32}\ (\gamma/\mu) \tag{23}$$

where K = hydraulic conductivity
e = void ratio
U = uniformity coefficient (ratio of D_{60} to D_{10})
D_{10} = grain size diameter having 10% of grains smaller
γ = specific weight of fluid
μ = dynamic viscosity of fluid.

Green and Corley (1971) studied several predictive models for the calculation of the hydraulic conductivity of porous media. Their equations were based on the work of Marshall (1958) and Millington and Quirk (1960), with the introduction of a matching factor (measured saturated conductivity ÷ calculated saturated conductivity). The modified equations adequately predicted the experimentally measured values and provided satisfactory conductivity data for many applications.

Johnson (1963) used laboratory permeability and geological data to predict the transmissibility of water over large areas where obtaining actual data from well testing was not economically feasible. Based on the relationship of particle size to permeability, he prepared graphs and tables for predicting permeability where data were not available.

Zanker (1972) developed a nomograph for the determination of hydraulic conductivity and intrinsic permeability in a laboratory water-soil system, based on common parameters such as length of the soil sample, volume of leachate, the differential head, the area of the sample, the duration of observation and the temperature of the water.

Although the above empirical formulae and relationships provide a means to estimate the coefficient of permeability, in general they are not applicable to clay-soils. The bound water associated with clays is thought to be the primary factor responsible for the inapplicability of these relationships. Because of this bound water on clays, seepage occurs only through a part of the pore space.

The effect of sorption on the movement of ions through exchange columns and on the mobility of pesticides in soils has been reported in the literature. Hashimoto et al. (1964), for example, defined a retardation factor, R, as:

$$R = 1 + P\,K\,N\,C^{N-1}/\theta \tag{24}$$

where P = bulk density of the column,
$K \& N$ = constants in the Freundlich equation ($S = KC^N$), (S = amount sorbed per unit mass of solid)
C = equilibrium concentration, and
θ = column water content.

Since R appears in the denominator of a general transport equation (Hashimoto et al., 1964), the larger its value, the more slowly the solute moves.

That a given organic solvent moves through soil at a rate which depends upon its distribution between an aqueous phase and the soil itself has been demonstrated by Briggs (1973), who reported a linear relationship between log ($1/R_F-1$) and log Q, where R_F is the retention factor for an unionized pesticide (obtained from soil thin layer chromatography), and Q is the soil organic matter÷water partition coefficient. Briggs has taken the analysis a step further and developed an equation relating R_F to the octanol/water partition coefficient, P (see subsequent discussion).

Changes in Permeability With Time

Several investigators have reported on changes in the measured coefficient of permeability as a function of time. Bodman (1937), for example, observed in laboratory column tests on California soils that the permeability "constant" decreased with time, precipitously for the first 20 days and gradually thereafter. Rates of decrease were found to correlate closely with silt content, whereas final permeabilities were related to the percentage of clay-size material in the sample. Based on a study of the conductivity of the percolate, Bodman concluded that the permeability decrease could be attributed to leaching of electrolytes from the soil, and consequent arrangement of particles into conducting pores.

In a later, more detailed study of this phenomenon, Poulovassilis (1972) concluded that changes in pore volume and geometry, while important, were responsible for only 15 percent of the decrease in permeability. Of greater significance was the evolution and entrapment of gases of microbial origin which had the effect of clogging pores and thus of reducing permeability by as much as 83 percent of the original value. Earlier, Allison (1947) had recognized that microorganisms were responsible for decreased permeability in submerged soils and attributed this to the natural clogging of soil pores by cells, slime and products of microbial growth.

ATTERBERG LIMITS

Physical properties of clay are critically dependent on moisture content; a clay may exhibit liquid or plastic behavior depending on how much water it contains. The water contents which characterize the onset of liquid and plastic behavior and which characterize soil or clay saturation are referred to as the Atterberg limits. The significance of these limits was noted by Terzaghi (1926) when he wrote, "The results of the simplified soil tests (Atterberg limits) depend precisely on the same physical factors which determine the resistance and the permeability of soils (shape of particles, effective size, uniformity) only in a far more complex manner."

The liquid limit (W_ℓ) is that water content above which the particles of a soil are no longer held together by attractive, cohesive forces, that is at this limit or water content, the soil behaves like a viscous fluid or paste. Yong and Warentin (1975) defined the plastic limit (W_p) as, "...that water content below which the soil is no longer plastic when it is worked, and crumbles on application of pressure". The plastic limit can be interpreted as the lowest water content where cohesion of particles is low enough to allow movement but high enough to permit particles to maintain their positions after remolding. The shrinkage limit (W_s) is the smallest amount of water that can completely saturate a soil.

Kezdi (1974) indicated that typical values of W_ℓ ranged from 40 to 150 and values of W_p from 25 to 50 for clays. The range of water content between the liquid and plastic limits is called the plasticity index, I_p, and for clays this extends between 10 and 100 (Kezdi, 1974). In general, the greater the plasticity index, the greater the swelling potential of a clay (Mitchell, 1976). A graphic summary of Atterberg limits is given in Figure 4.

CLAY-ORGANIC STUDIES: X-RAY INVESTIGATION OF SWELLING

It is commonly known that expandable layer silicates are capable of forming interlayer complexes with water and with organic molecules and that the characteristic spacing between the layers is dependent upon the nature of the intercalated molecule. Greene-Kelly (1955) has observed, for example, that the d(001) spacing in montmorillonite can vary from 9.5 Å when unexpanded, to 23.3 Å in the presence of pyridine. In his orientation studies with aromatic compounds, Greene-Kelly (1955) concluded that molecules could orient themselves either parallel or perpendicular to the silicate sheet and that the preferred orientation depended upon the external concentration.

Olejnik *et al*. (1974), who investigated the swelling of montmorillonite in polar organic liquids, obtained much larger interlayer spacings, particularly for substances which have high dipole moments and high dielectric constants such as formamide. In general, the degree of swelling observed for a variety of homoionic, alkali metal montmorillonites, was not in keeping with expectations based on Norrish's (Norrish, 1954) swelling index. According to Norrish (1954), swelling should be related to UE/v^2, where U is the solvation energy (i.e., the amount of heat given off when water or an organic molecule interacts with an interlayer cation), E is the dielectric constant of the interlayer liquid, and v is the valence of the interlayer cation. The failure of this relationship has led Olejnik *et al*. (1974) to conclude that the measured bulk dielectric constant of a liquid, and the actual dielectric constant of that same liquid in the interlayer region of a clay, might be radically different. Still, as Barshad has observed (Barshad, 1952), the dipole moment and the dielectric constant can be effective predictors of swelling behavior. This point will be returned to in the discussion of swelling presented in this report.

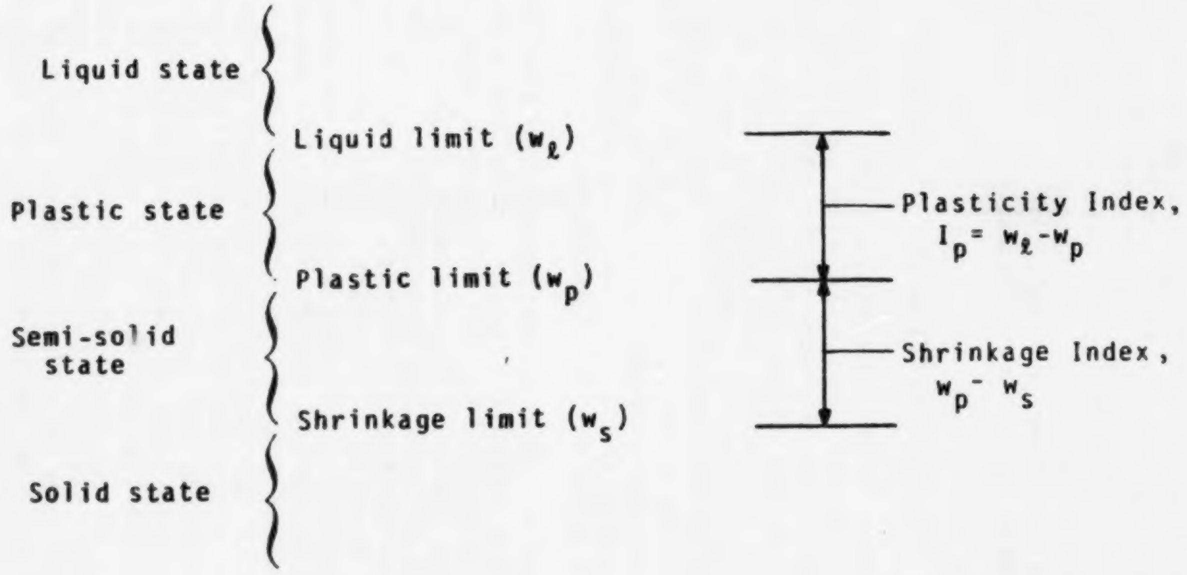

Liquid state
Liquid limit (w_ℓ)
Plastic state
Plastic limit (w_p)
Semi-solid state
Shrinkage limit (w_s)
Solid state
Plasticity Index, $I_p = w_\ell - w_p$
Shrinkage Index, $w_p - w_s$

Figure 4. Atterberg Limits and Indices

An extensive review of clay-organic interactions can be found in Theng's book *The Chemistry of Clay-Organic Reactions* (Theng, 1974). The nature of clay-organic complexes, including the effect of organic molecules on interlayer spacings, is discussed for alcohols, polyhydroalcohols, ketones, aldehydes, ethers, nitrites, amines, aliphatic and aromatic hydrocarbons, organic pesticides and positively charged organic species. Of interest here is Theng's observation that even in dehydrated clays, intercalation of non-polar organic molecules either does not occur at all, or proceeds only with great difficulty. This is reasonable since substances such as benzene would be only weakly adsorbed and would therefore be incapable of expanding the silicate layers.

In this connection, Barshad (1952) has observed, using X-ray diffraction, that benzene and n-hexane intercalated with some montmorillonite samples after these had been dehydrated at 293°K, but did not intercalate when the samples had been dried at 523°K. McEwan (1948) observed no intercalation with n-hexane and n-heptane, even after the air-dried samples of montmorillonite had been boiled in the hydrocarbon liquids. Benzene, however, did form a double-layer complex after this treatment. This is in contrast to the results of Greene-Kelly (1955) who used a similar technique (where montmorillonite was dried at 353°K) but failed to achieve intercalation. The record is somewhat mixed on efforts to form clay-organic complexes with molecules having low polarity.

It should be pointed out that while a considerable literature exists on interlayer swelling of clays in organic liquids, no one has reported on the shrinkage or swelling of bulk quantities of clay in contact with organic solvents, using the consolidometer method employed in the current study. For the most part consolidometer studies have been confined to aqueous clay systems in connection with ground swell potential, failure of structures, highway maintenance, etc. To the knowledge of the authors, this investigation is the first systematic study of mechanical shrink-swell behavior using organic liquids.

OCTANOL/WATER PARTITION COEFFICIENT

Early studies on the partitioning of organic substances between water and an apolar phase were conducted independently by Mayer and Overton who were interested in the effect of organic compounds in producing anesthesia and narcosis (Hansch, 1974). They were able to show that the potency of a narcotic is directly related to the extent to which the compound partitions itself between olive oil and water, that is, to its olive oil/water partition coefficient. Mayer and Overton reasoned that since nerves are surrounded by fatty membranes, the more fat soluble compounds would partition into these and disrupt nerve operation more effectively than drugs with an affinity for the aqueous phase.

Hansch and Elkins (1971) found a more satisfactory relationship to exist between medicinal properties and the octanol/water partition coefficient, P, defined as

$$P = \frac{\text{concentration of solute in n-octanol}}{\text{concentration of solute in water}} \tag{25}$$

Hansch et al. (1968) also reported that an excellent linear correlation exists between the logarithm of the aqueous solubility of organic liquids and log P as given in the equation:

$$\log (1/S) = a \log P + b \tag{26}$$

where S is the molal solubility of the organic liquid in water; P is the partition coefficient of the liquid between 1-octanol and water; and "a" and "b" are constants. In general, the lower the solubility of a substance in water, the greater its partition coefficient, P.

Chiou et al. (1977) reported an empirical correlation between the aqueous solubilities of a variety of potential environmental contaminants (including aromatic hydrocarbons; organophosphate and organochlorine pesticides; and polychlorinated biphenyls (PCB's))and the n-octanol/water partition coefficients of those contaminants. More importantly, they also showed that a good correlation exists between the bioconcentration factor of an organic pollutant in rainbow trout and the aqueous solubility of the pollutant, according to the equation:

$$\log (\text{B.F.}) = 3.41 - 0.508 \log S \tag{27}$$

where B.F. is the bioconcentration factor and S is the aqueous solubility (μ moles/l). Thus, it is now possible to use widely available solubility or partition coefficient data to predict the uptake of certain organic pollutants by certain aquatic organisms.

More pertinent to the present study is the finding by Briggs (1973) that there is a relationship between the octanol/water partition coefficient for unionized organic compounds and their adsorption on and movement through soils. Using R_F (retention factor for unionized pesticide) as an index for the mobility of organic chemicals through soils, Briggs has classified compounds into five types, ranging from immobile to very mobile, and has shown that in general immobile compounds are those which have high values for log P (>3.78), and very mobile compounds are those with low values (Log P < 0.08). This suggests that the rate of movement of an unionized organic substance through water-containing soils can be related to the tendency of the substance to escape from the interparticle aqueous phase and to become sorbed onto the immobile soil particle itself. The greater this escaping tendency as measured by log P, the lower the mobility of the organic substance. (See discussion of sorption and permeability).

SECTION 5

METHODS

INTRODUCTION

This section of the report presents the experimental procedures for studies on those properties of clays which might influence their ability to augment or alter the transmission of fluids.

Three clay-soils and one soil sample were initially selected for study, but, for a variety of reasons, only the three clay-soils (without deflocculent) were used extensively in tests with organic solvents (ACS grade or equivalent). Samples of the three clay-soils, Ranger Shale, Kosse Kaoline, and Fire Clay, were obtained from a commercial clay supplier. The soil sample was collected from Parker, Texas (Collin County). The Parker sample was obtained using an auger, from a depth of about 8 feet ($\sim$2.5 m), which was well below the third soil horizon.

CLAY MINERALOGY

Clay minerology for Ranger Shale, Kosse Kaoline, and Fire Clay was determined at the Colorado School of Mines Research Institute. Oriented mounts were prepared, scanned over 3 - 31° of 2θ, glycolated and then rescanned over the same range to determine expandable clays. Parker soil was examined in the UTD laboratory using glycolation as discussed in Pierce and Siegel (1969) and in Biscayne (1965).

PARTICLE SIZE ANALYSIS

Fifteen to 25 grams of sample clay were measured into a 250 ml Erlenmeyer flask containing 100 to 150 ml of distilled water. The flasks were stoppered with Parafilm, placed on a gyroshaker and shaken at 250 rpm for 12 to 16 hours. The rotating motion of the table gently disintegrated the sample without significantly reducing the individual particle sizes. The sample was then quantitatively transferred to a one liter glass cylinder. One gram of Calgon was added as a deflocculant. Some samples were run without Calgon to compare results of flocculated and deflocculated samples. After thorough stirring, the mixture was allowed to stand for 24 hours to be sure it showed no signs of flocculation. If flocculation was observed, the amount of Calgon was increased. If no signs of flocculation were observed the mixture was again thoroughly stirred; when stirring was ceased, time was recorded. The settling velocity of a particle 2 μ in diameter was determined according to Stokes' Law (Black, 1965). Time required for particles $\leq 2\ \mu$ diameter to settle a distance of 10 cm was then calculated. After settling for the calculated time, a 20 ml sample was drawn with a pipette from a depth of 10 cm so that it contained particles about 2 μ in diameter. The subsample was transferred into a beaker of known weight, evaporated at 110° C for 24 hours and reweighed.

The clay size fraction was determined from the following relationship:

$$w/w_o = P/100 \tag{28}$$

where w = weight of particles present in the volume at time, t;

w_o = weight of particles in the volume initially;

P = percentage of particles by weight, of size 2 micron and smaller.

The sand fraction was determined by pouring the rest of the sample through a number 40 sieve, washing it with distilled water and collecting the residual material in a preweighed beaker. This material was dried at 110°C for four hours and reweighed. The weight of clay was taken to be of size 2 micron and less and the weight of the sand was determined as the dried material retained on the number 40 sieve. Silt was calculated to be the remainder of the sample.

MOISTURE-DENSITY RELATIONSHIPS

The Harvard Miniature Compaction Apparatus manufactured by Soiltest, Inc., Evanston, Illinois, was used to determine the moisture-density relationships and optimum moisture content of the test clays. The Harvard Miniature Compaction test is a method suggested by the American Society for Testing and Materials (ASTM) for determining moisture-density relationships of soils (Soiltest, Inc., 1976). The test determines the relationship between the moisture content of soils and resulting densities (oven-dry weight per volume) when the soil is compacted in the laboratory with this apparatus giving maximum dry density. The Harvard Miniature Compaction Apparatus closely approximates the action of the sheepfoot roller (Soiltest, Inc., 1976). Its mold capacity is 1/454 cu. ft (62.3 cm^3). The procedure followed for determining moisture-density relationships was taken from ASTM (1970) and is outlined below.

Each sample was prepared by air drying two to three pounds of the clay sample to a slightly damp condition. Lumps were broken and then homogenized so that the material passed through a number 40 sieve. The sample was then divided into 6 to 8 portions, such that each portion contained slightly more than enough material for one test. To each portion, the approximate required amount of water was added to obtain the desired range of moisture content. After thoroughly mixing, each portion was placed in a small glass jar tightly fitted with Parafilm and stored overnight or until ready for testing. For samples that mixed readily with water and had low dry strength, it was satisfactory to add water and mix the specimen immediately prior to testing. A compacted specimen should not be remixed and used over again.

Prepared clay was put in the mold. The surface was leveled using a wood plunger. The tamper was inserted in the mold until it was in contact with the surface of the soil, and pressed down until the spring began to compress. After the force was released, the tamp was shifted to another position. Each of the four tamps was applied in a separate quadrant, adjacent to the mold. The fifth tamp was in the center, making one complete coverage. This cycle was then repeated until the appropriate number of tamps had been applied. Ten tamps with a 20 lb. (9 kg) spring were needed for the standard low compaction test. The tamps were applied at the approximate rate of 10 tamps per 15 seconds.

The next layer of sample was added and the procedure repeated until the required number of compacted layers had been placed in the mold. The top layer extended at least 1.3 cm into the extension collar.

The mold assembly was then transferred to the collar remover. The mold was removed from the base and the excess soil from the top of the mold was trimmed away. The sample from the mold was removed with the ejector and was placed in a preweighed container and reweighed.

The sample was then dried in an oven at 110°C for 24 to 48 hours. Drying was continued to constant weight. If the specimen was used for a permeability test it was either done at known moisture content or the moisture content was determined from the excess material removed from the collar. Additional specimens were compacted until points had been established on both sides of the optimum moisture content curve.

ATTERBERG LIMITS

Atterberg Limits were determined using methods for finding liquid limits and plastic limits for soils by the American Association of State Highway Officials designations T-89 and

T-90, respectively (Black, 1965). For the liquid limit test, Standard Liquid Limit Device (CL-207) manufactured by Soiltest, Inc., Evanston, Illinois, was used. For the plastic limit test, Plastic Limit Set (CL-251) by Soiltest, Inc., Evanston, Illinois, was used. The standard liquid limit device was made of hard rubber to maintain the uniformity of hardness, size and density of all devices. The brass cup was die-formed to specified dimentions. The cup and drop adjustment parts and aluminum hand crank were mounted on an aluminum housing.

Determination of liquid limit was based on the number of drops of the standard tamp needed to close the gap made in the clay with the standard grooving tool and the corresponding moisture content of the clay. The number of blows needed at various ranges of moisture content were determined and the values were plotted as the log of the number of blows versus moisture content. This relationship was found to be linear. The liquid limit was determined from the graph, as the moisture content at 25 blows.

Determination of plastic limit was based on the moisture content of the clay which crumbled at the surface as the clay sample was rolled narrower than 1/8" (3.2 mm) diameter. It was determined by the use of the standard plastic limit plate.

SPECIFIC GRAVITY

Specific gravity was obtained by a standard procedure using a pycnometer. It was calculated from the mass volume of the sample. The mass was determined by weighing and the volume by calculation from the mass and density of water displaced by the sample.

CATION EXCHANGE CAPACITY

Cation exchange capacity was determined from the procedure of Busenberg and Clemency (1973) using an ammonia specific ion electrode. The procedure, which requires saturation of the exchange sites with ammonium ion, utilizes the electrode in the determination of ammonia released by treatment of the ammonium-saturated clay with strong base. The procedure is as follows:

Ammonium-saturated clay samples were prepared by placing the sample in an excess amount of a 1 N ammonium acetate solution and shaking on a gyroshaker for 16 to 20 hours. The solution was adjusted to pH 7 and was transferred to a 50 ml centrifuge tube. It was centrifuged at 24,000 g for 10 minutes. The supernatant was then decanted. A 1 N ammonium chloride solution was added and the mixture was shaken for 5 minutes. After recentrifuging, the supernatant was decanted. This procedure was repeated four times.

Excess ammonium salts were removed by washing with isopropyl alcohol. Isopropyl alcohol was added, the mixture was shaken, centrifuged and the supernatant decanted. This procedure was repeated four times. After the clay was air dried, it was ready for CEC determination. One gram of air dried (treated) clay was placed in a 150 ml beaker and 100 ml of deionized water were added and the mixture was stirred well. Then 1 ml of a 10 M sodium hydroxide solution was added. After about a minute, the released ammonia was measured by the Orion Specific ion ammonia electrode method.

Calculation of CEC

The CEC of the sample was determined by the following equation:

$$CEC = (c)(v)/(w)(f) \qquad (29)$$

where CEC = Cation Exchange Capacity of the sample in meq/100 g clay
c = concentration of ammonia in moles/liter
v = volume of water added in ml
w = weight of the sample in mg
f = conversion factor, in this case a constant equal to 10^{-5}.

Exchangeable Cations

Exchangeable cations were identified by treating 10 g of distilled water washed clay with 1 N NH_4 Cl overnight. The resulting solution was analyzed for Ca and Mg by titration (APHA et al., 1976) and for Na and K by flame photometry using a Corning Model 430 Flame Photometer.

TOTAL CARBON AND CARBONATE ANALYSIS

Total carbon content of the clay sample was determined in the IR-12 Carbon Determinator (Leco Corporation, St. Joseph, Michigan). For carbonate analysis, total carbon was determined on acidified samples. About 5 grams of sample were acidified with dilute HCl (20%) in a porcelain crucible until no further bubbling of CO_2 occurred. The operation was repeated several times until bubbling completely stopped. The sample was then air dried and analyzed for total carbon on the IR-12 carbon analyzer. The difference between total carbon content of unacidified and acidified samples was equal to the carbonate carbon content.

SWELL PROPERTIES

Swell properties were measured (using remolded clay) with a 6.4 cm diameter consolidometer manufactured by Karol-Warner, Inc., Highland Park, N.J. The dial indicator on this insturment was capable of measuring displacements up to one ten thousandth of an inch (2.5×10^{-4}cm). Studies involving organic solvents were run in a desiccator to prevent evaporation and, in the case of mixtures, changes in solvent composition. Experiments were conducted in a constant temperature room at 22 ± 1°C. The detailed procedure adapted from ASTM (1970) is given below.

A 500 to 600 g aliquot of well-ground (passed through a No. 8 sieve), air-dried sample was weighed and transferred to a mixing pan. The amount of deionized water required to achieve the optimum moisture content of the clay was added to the clay sample. After thorough mixing, the sample was placed in a glass jar tightly fitted with Parafilm and stored overnight or until ready for testing. For samples that mixed readily with water and had low dry strength, it was satisfactory to add water and mix the sample immediately prior to testing. It is important that a compacted clay not be remixed and used over again. A specially designed mold (7.6 cm long, 6.0 cm inner diameter) and collar (7.6 cm long) were used to make the remolded clay sample. With the mold and collar clamped to the base, about half of the mixed clay was placed in the mold. The surface was leveled with a wood plunger. The sample was then compacted with a 5.5 lb. (2.5 kg) standard hammer to conform to the standard compaction test procedures (12,375 ft. lb. per cu. ft. (5.9×10^5 joules/m^3) of compacted volume). About 10 to 20 percent additional pressure was applied depending on the amount of excess volume of compacted clay. After removing the collar and shaping the sample with a straight edge, the sample was ejected with a specially designed plunger.

A 3/4 in. (1.9 cm) long sample was then cut and shaped properly using a sharp knife and a straight edge. A 1.9 cm long collar was used to create a fine and precise finish on the sample. The molded sample was then transferred to a specially designed consolidometer (3.8 cm long, 6.4 cm inner diameter) over a 0.6 cm thick porous stone. Another piece of porous stone of the same size was placed at the top of the sample. A load block was then placed at the top. A dial gage indicator capable of measuring within a range of 0.0001 to 0.5 inch (0.002 to 13 mm) was mounted in proper position. To read any possible shrinkage of the sample the dial gage indicator was adjusted to read initially at 0.01 to 0.02 in. (0.025 cm to 0.05 cm). If more shrinkage was expected, the dial gage was initially adjusted accordingly. The consolidometer was transferred to a desiccator (without the desiccant). Fluid was then introduced up to a level 1.5 cm above the consolidometer, that is, samples were flooded with the fluid. Wall friction in these experiments was assumed to be negligible. Measurements of the swell or shrinkage of the sample were made as a function of time.

COEFFICIENTS OF PERMEABILITY FOR LIQUIDS AND LIQUID MIXTURES IN CONTACT WITH CLAYS

In this study the coefficients of permeability were determined on remolded clay using a laboratory apparatus with heavy-duty permeameter columns (see Figure 5). These permeameters were

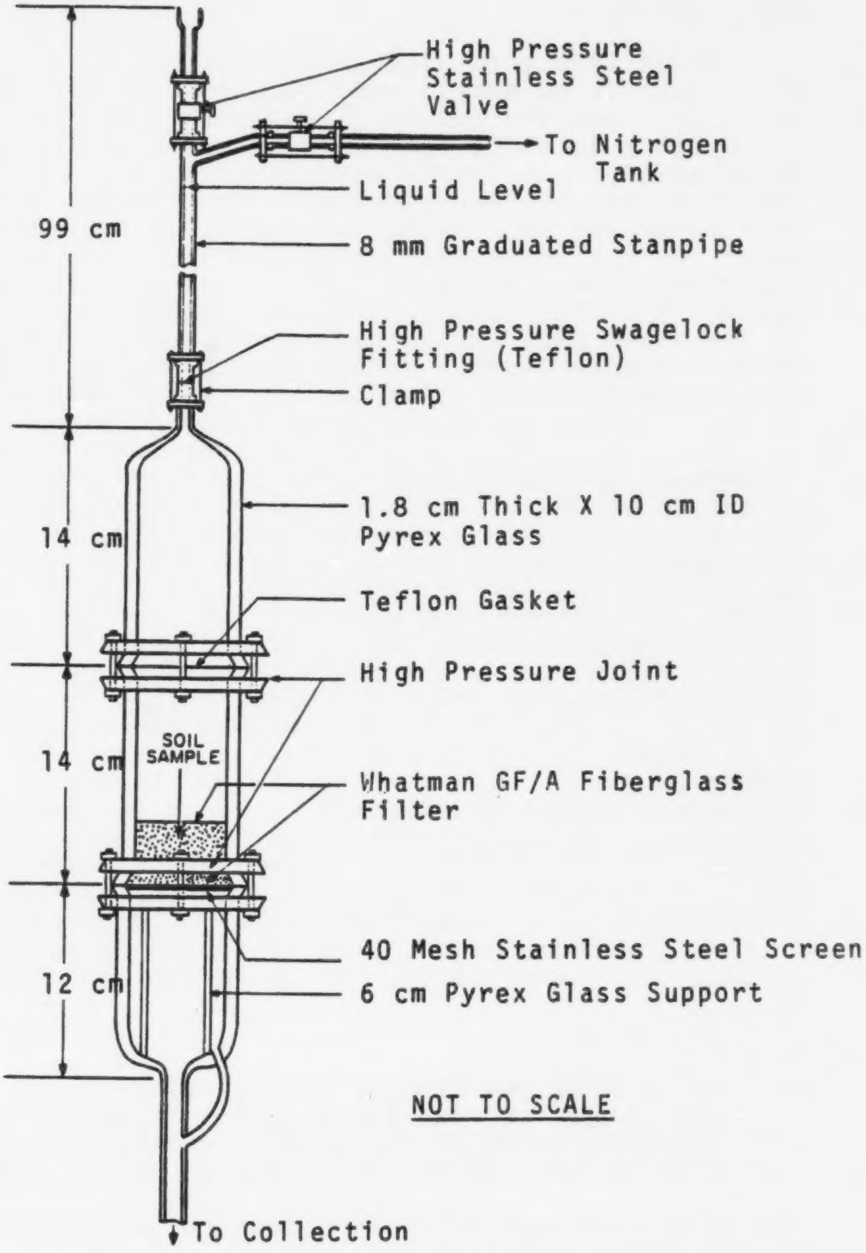

High Pressure Stainless Steel Valve
To Nitrogen Tank
Liquid Level
8 mm Graduated Stanpipe
High Pressure Swagelock Fitting (Teflon)
Clamp
1.8 cm Thick X 10 cm ID Pyrex Glass
Teflon Gasket
High Pressure Joint
SOIL SAMPLE
Whatman GF/A Fiberglass Filter
40 Mesh Stainless Steel Screen
6 cm Pyrex Glass Support
99 cm
14 cm
14 cm
12 cm
NOT TO SCALE
To Collection

Figure 5. Pressure permeability column

designed and built with Pyrex glass in the University of Texas-Dallas machine shop especially for this study. All joints in the columns were lined with Teflon to make them suitable for use with organic solvents. The procedure followed for determining the coefficient of permeability, adapted from ASTM (1970), is given below.

About 1000 g to 1200 g of well-ground (pass through a No. 4 sieve) air-dried sample were weighed and transferred to a mixing pan. The required amount of deionized water corresponding to the optimum moisture content, was added to the clay sample. After mixing, the sample was placed in a glass jar, fitted with Parafilm, and stored overnight. For samples that mixed readily with water and had low dry strength, it was satisfactory to add water and mix the specimen immediately prior to testing. It is important that a compacted specimen not be remixed and used over again. With the mold and collar clamped to the base, about half of the mixed clay was placed in the mold. The surface was leveled by pressing lightly with a wooden plunger. The sample was then compacted with a 5.5 lb. (2.5 kg) standard hammer to conform to the standard compaction test procedures (12,375 ft. lb. per cu. ft. (5.9×10^5 joules/m^3) of compacted volume). About 10 to 20 percent additional energy was applied depending on the amount of excess volume of compacted clay. Actual moisture content of the clay sample was determined separately, by oven drying a duplicate sample at 110°C for 24 hours. The excess clay in the mold was scraped and leveled carefully up to the 2 in. (5 cm) mark depth. The molded clay was ready for testing in the permeability column, which was then assembled and test fluid introduced. Final fluid level in the graduated standpipe was adjusted very precisely with the help of a pipet bulb. Temperature measurements of the fluid were taken with a thermometer well immersed in a reagent bottle filled with the fluid. The open end of the standpipe was firmly covered with two layers of Parafilm and a hypodermic needle was inserted through the Parafilm. Using this technique, evaporation of solvent was reduced to an insignificant amount. If any clay-fluid system had a coefficient of permeability less than 10^{-10} cm/sec, the open end of the standpipe could be attached to a pressurized nitrogen tank and a constant pressure in the range of 10 to 50 psi could be maintained. The coefficient of permeability 'K' in cm/sec was computed as:

$$K = QL/AH \tag{30}$$

where Q is the flow of the percolate in ml per second, L is the height of the sample in the column in cm, A is the cross sectional area of the sample in square cm, and H is the average head of the fluid medium on the sample in cm.

The void ratio was calculated from the actual moisture content of the compacted clay.

X-RAY DIFFRACTION STUDIES OF CLAYS IN CONTACT WITH SOLVENTS AND SOLVENT MIXTURES

Clays (< 2 µ diameter) separated by settling according to Stokes' Law were used to study the effect of organics on lattice spacing. Approximately one gram of the separated clay was measured into a 250 ml Erlenmeyer flask containing 100 ml of treatment solution.* The flask was then placed on a gyroshaker and run for 12 to 18 hours at 250 rpm. The clay solution was subsequently transferred to a polypropylene tube and centrifuged at 36,000 g for fifteen minutes. After centrifuging, the supernatant was decanted and the wet clay at the bottom of the tube was smeared onto glass slides to form a thin, smooth coating. The slides were then allowed to air dry for several minutes. After drying, they were run in a Norelco X-ray diffractometer and scanned at 2° 2θ per minute from 2° to 30° 2θ with copper radiation. The 2θ values of the peaks were converted to clay lattice spacing in Å.

Initially, difficulties were encountered in obtaining X-ray data for clays in contact with the neat organic liquids. Ranger Shale treated with benzene, for example, formed a stiff mass which did not adhere to glass. It was found, however, that adding three drops of distilled, deionized water to the centrifuged clay (as recommended by Hoffmann and Brindley, 1960) facilitated adhesion. The clay was then dried in a desiccator over P_2O_5 for 15 hours, and X-ray patterns obtained.

DETERMINATION OF MAJOR IONS

Three clay samples were sent to the University of Texas-Dallas Applied Research Laboratory where they were examined for major ions using the electron microscope. Intensities of characteristic X-ray lines were compared with the intensities from reference oxide standards for Si, Al, Ca, Fe and K.

DETERMINATION OF SORPTION ISOTHERMS FOR VOLATILE ORGANICS

Considerable time was spent in developing a method for obtaining reliable sorption isotherms, particularly for the highly volatile hydrophobic compounds being used in this investigation. A review of the literature revealed a few helpful references on this subject, although Sanks et al. (1975) did point out some of the difficulties which they encountered in their unsuccessful efforts to plot Freundlich isotherms for benzene on several clays. Although there are a number of papers which discuss the sorption of organic compounds from dilute aquatic solutions, no successful work has been reported for highly volatile organic solutes.

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*Baker Analyzed Reagent Grade Solvents.

Originally, it was proposed to conduct sorption studies with 25 grams of clay mixed with 75 ml of solution in a 250 ml Erlenmeyer flask. The extent of sorption was to be determined by measuring the difference between initial and equilibrium organic carbon concentrations with the Beckman Total Carbon Analyzer. However, in a series of experiments using benzene and Ranger Shale, several very serious sources of error were encountered which necessitated extensive modifications of the technique.

Despite the fact that Ranger Shale had a low organic carbon content, 0.28 percent, there was sufficient organic material leached from the clay to interfere with analysis. The presence of humic acids and other carbon-containing compounds in solution gave apparent equilibrium concentrations which were erroneously high. In some cases, where sorption was low, the equilibrium concentration actually exceeded the concentration of the standard solution. The problem was solved by using gas chromatography which separated the compound of interest from interfering substances.

A second, somewhat more subtle, problem in working with volatile organics was loss of vapor to the air space above the solution. Initially, it was thought that the quantity of benzene, for example, lost to the air space would be insignificant when compared to the amount sorbed by the clay. However, as the following calculation shows, vaporization to the air space can be appreciable:

Suppose that 50 ml of an aqueous benzene solution having a concentration of 1.52×10^{-3} M is placed in 100 ml volumetric flask capped with a ground glass stopper, and that the temperature is 20°C. The initial number of moles in the system is 76×10^{-6} moles. The molecules will distribute themselves according to Henry's Law which can be written as:

$$P/c = k \qquad (31)$$

where P = partial pressure in atmospheres of benzene over the solution,
c = concentration in moles/l, and
k = 4.22 (Atm/mole) (at 20°C) (Green and Frank, 1979)

If n_ℓ is the number of moles of benzene in the liquid and n_g is the number of moles in the vapor phase, then the following equations must be satisfied:

$$n_\ell + n_g = 76 \times 10^{-6} \qquad (32)$$

and

$$P/C = (n_g RT/V_g)/(n_\ell/V_\ell) \doteq \{(n_g)(82.02)(293.18)/50\}/(n_\ell/0.05)$$

$$= 480.9\ n_g/(n_\ell/0.05) = 4.22 \qquad (33)$$

where V_g = volume occupied by the vapor in cm^3, and

V_ℓ = volume of the solution in liters.

Solving for n_ℓ gives 64.7×10^{-6} moles or a concentration of 1.29×10^{-3} moles/l in the liquid phase. Under these conditions, a concentration change of 0.23 mmoles/l can be expected as a result of vaporization alone. This is comparable to the amount sorbed by the clays. Consequently, it is necessary to minimize air space above the liquid.

While the escaping tendency for hydrophobic solutes is higher than for acetone which hydrogen bonds with water, the vapor pressure of acetone over aqueous solutions at low concentrations is also sufficiently high to warrant reduction of air space above the liquid to a minimum. For example, at a concentration of 2000 mg/l (mole fraction = 6.2×10^{-4}) the partial pressure of acetone is 0.714 torr (Washburn, 1923).

A technique was developed for obtaining satisfactory isotherms for volatile solutes which involved taking a number of precautions to prevent evaporative losses. Standard solutions were prepared by using a variation of Marketos' method (Marketos, 1969) in which a small quantity of the solute (ranging from 50 to 2000 mg) was weighed into a 5 ml capped vial. The vial was immersed in a dry ice-acetone slurry (for acetone, liquid N_2 should be used) to freeze the contents. Once the liquid was solidified, the cap was removed and the vial contents were quickly transferred to a volumetric flask filled with one liter of carbon free water and containing a stirring bar. Following the practice of Bohun and Claussen (1951) in their studies of hydrocarbon solubilities in water, the ground glass cap of the flask was coated with silicone grease and securely taped. The volumetric flask was then inverted a number of times to insure mixing and the flask was placed on a magnetic stirrer for 24 hours.

Chilled stock solutions were transferred in a cold room to a re-pipette bottle and an accurately measured volume of the solution was added to a flask containing a weighed amount of clay. For both acetone and the hydrophobic organic compounds, 10 to 25 grams of clay per 100 ml of stock solution gave equilibrium concentrations 5 to 50 percent lower than the stock solutions.

Flasks with the taped, silicone-coated stoppers which contained the clay, the solution, and several steel balls (to prevent settling) were placed on a gyroshaker and swirled at 150 rpm for 24 to 48 hours. The equilibration time used in this work is consistent with the procedures of Hoffman and Brindley (1960), Huang (1971), and Aly and Faust (1964) and with observations in the current study that benzene sorption on Ranger Shale is essentially complete within six hours (see Figure 6).

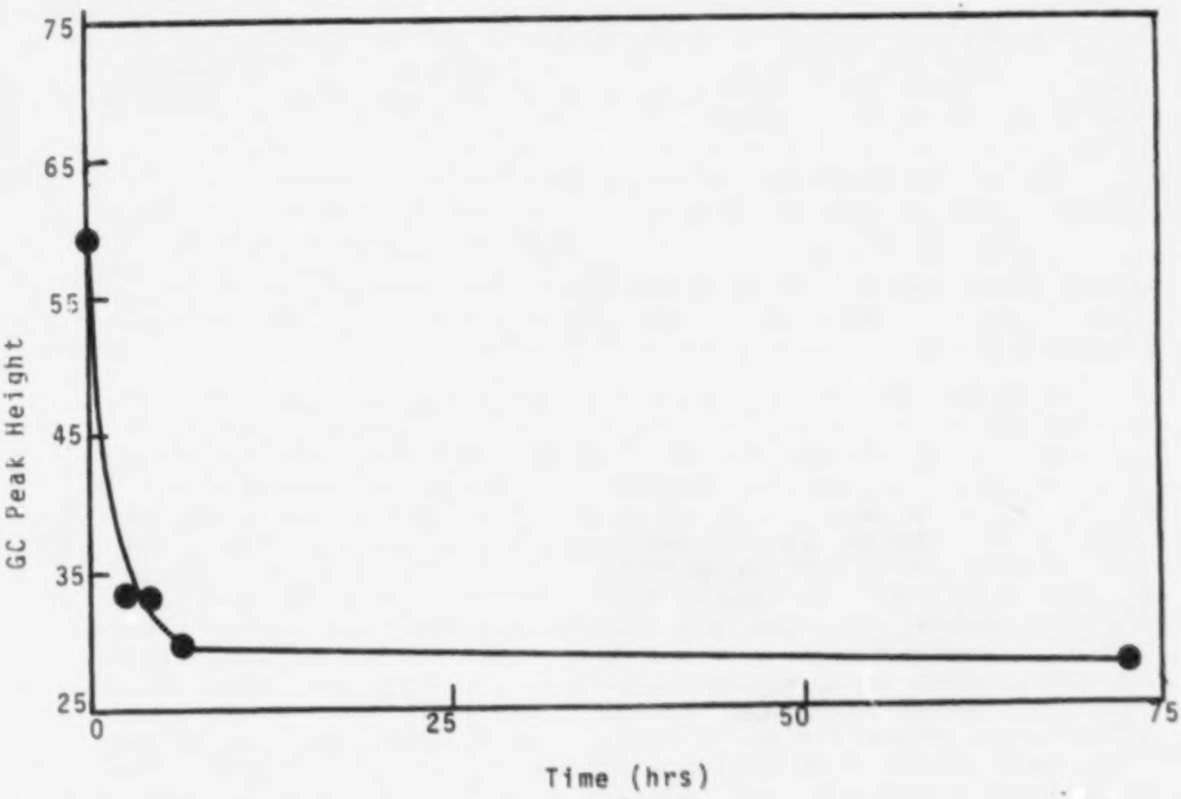

Figure 6. Change in peak height (concentration) with time for benzene sorbed onto Ranger Shale

An alternative procedure which also gave good results involved the use of stoppered bottles with ground glass caps.

Mixing was accomplished by magnetic stirring in this case. After equilibration, mixtures were transferred to polypropylene centrifuge tubes, care being taken to avoid air space above the mixture. Centrifugation was carried out at 5°C for five minutes at 43,000 g. At this temperature, no evaporative loss of benene or xylene was detected for solutions run in the absence of clay. The time required for essentially complete compaction of the clay was about one minute; during this period the temperature of the solution fell 2 to 3°C. It is unlikely that a significant shift in the equilibrium concentration, which is reported for 24 ± 3°C, took place under these conditions. The clear supernatant was analyzed using a Varian gas chromatograph with a flame ionization detector. Table 1 lists the conditions for analysis.

TABLE 1. CONDITIONS FOR ORGANIC SOLVENT ANALYSIS

Compound	Packing	Gas Flow Rate (cc/min)	Oven Temp (°C)	Relay Time (Min)
Acetone	Chromasorb W	30	110	1.25
Benzene	Chromasorb W	30	110	1.6
m-xylene	Chromasorb W	30	110	2.0
Carbon Tetrachloride	Chromasorb W	50	140	0.5

Throughout the course of this investigation, improvements in the method which might allow for more expeditious collection of data or for better analytical precision were constantly sought. In the last months of the project, 50 ml stainless steel centrifuge tubes equipped with O-rings were used to equilibrate and centrifuge the samples in the same container, thus eliminating one of the transfer steps.

A recommended procedure consistent with the above findings can be summarized as follows:

Weigh out three to fifty grams of clay into each of eight 50 ml stainless steel tubes. Place two 0.25 inch (0.6 cm) diameter stainless steel balls into each of the tubes to insure good contact between the clay and the organic solute. Add a measured amount of solution sufficient to completely fill the container; cap, and place on a gyroshaker at 225 rpm for a minimum of 24 hours. Without transfer, centrifuge at room temperature for 20 minutes on a Beckman Model J-21B centrifuge (cooling is not required with the stainless steel tubes). Then analyze the supernatant for organic compounds of interest using a gas chromatograph.

SECTION 6

RESULTS AND DISCUSSION

INTRODUCTION

Presented in this section are the characteristics of the clays used in this investigation; the results of the work on sorption of organics from dilute aqueous solutions onto clays; swelling of clays in water, organic solvents, and solvent mixtures; permeability of clays to water, organic solvents and solvent mixtures; and the behavior of clay lattices in contact with various liquids (X-ray diffraction studies). Also presented is a discussion of the results obtained on the effects of solvents and solvent mixtures on the characteristics of the clay and soil samples examined.

CHARACTERISTICS OF CLAYS USED IN THIS INVESTIGATION

Particle Size Analysis

Particle size distribution is an important parameter in characterizing the type of solid substrate. Size distributions for materials used in this study are presented in Table 2. The particle size distribution for Parker soil was obtained with and without Calgon polyphosphate dispersant in order to determine the effects of this material on particle size results. From the data in Table 2, it is evident that Calgon had a measurable impact on the particle size distribution of the Parker soil. As expected, the deflocculant caused an increased percentage of the clay particle size fraction.

Table 2 shows very high clay content (particles of size $\leq 2\mu$ without deflocculant) for all the samples except the Parker soil. In terms of clay fractions, the materials used in this study ranked in the following order: Kosse Kaoline > Fire Clay > Ranger Shale > Parker Soil. It should be pointed out, however, that the 2μ limit is somewhat arbitrary and that some clay minerals may exceed this size (Mitchell, 1976, p. 24).

Clay Mineralogy

While it is generally not possible to predict the behavior of clays and soils on the basis of their composition alone,

Table 2

PARTICLE SIZE DISTRIBUTION*

Sample	Clay	Silt	Sand
	Weight Percent		
Ranger Shale			
A	40	59	1
B	40	59	1
Fire Clay			
A	45	53	2
B	43	56	1
Kosse Kaoline			
A	57	43	0
B	49	51	0
Parker Soil			
A	10	70	20
B	11	71	18
Parker Soil (with deflocculant)			
A	18	66	16
B	22	58	20

A and B are duplicates.

*Unless otherwise noted, all samples were run without deflocculant.

clay mineralogy is of extreme importance in understanding the physical and chemical behavior of soils. Mitchell (1976, p. 71) has called attention to the dominating influence of the clay phase by noting that "In general, the greater the quantity of clay mineral in the soil, the higher the plasticity, the greater the potential shrinkage and swell, the lower the permeability, the higher the compressibility, the higher the true cohesion and the lower the true angle of internal friction."

Each of the clay minerals is characterized by a particular structure. Kaolinite consists of a silicate sheet (Si_4O_{10}) bonded to an aluminum-hydroxyl sheet in a two-layer structure in which replacement of the aluminum and silicon by other elements is rare. In montmorillonite, the aluminum-hydroxyl sheet is positioned between two silicate sheets stacked along the c-axis. This arrangement allows for variable water content between the layers; montmorillonite is known to expand in water and in other polar liquids. Because substitution of other elements such as iron, magnesium and zinc, for aluminum is possible, the chemical composition of montmorillonite is highly variable. Illite is a general term referring to a mixture of muscovite (a potassium-rich mineral) and montmorillonite, both of which are three-layered clays (Mason, 1958).

Results of the X-ray diffraction determination of clay mineralogy of the samples evaluated in this investigation are presented in Table 3. The clay fraction of the Parker soil was 10 percent by weight; approximately 50 percent of the clay was montmorillonite, 35 percent illite, and 15 percent kaolinite. The clay fraction of the Ranger Shale (50 percent by weight) was composed of a variety of clay types with about 10 percent being montmorillonite. The clay fractions of the Kosse Kaoline and Fire Clay were predominantly kaolinite with about 5 percent illite-mica and 10 to 16 percent quartz. The amount of expandable layer clays was low in all clay-soils evaluated.

Moisture-Density Relationships

The moisture-density relationships for the solids used in this investigation are plotted in Figures 7, 8, 9 and 10. These figures display a well-defined relationship between moisture and density. It has been found that the Harvard Miniature Compaction unit is easy to handle and requires a much smaller sample to perform the test of this type than the larger units normally used. It is sensitive to minor moisture changes. Its operation somewhat resembles methods used for compaction of clay liners for industrial waste disposal pits. The clay-soils used in this study for swelling and permeability measurements were packed at the optimum moisture content determined from these figures.

Table 4 presents the optimum moisture content and corresponding dry density for the solids under investigation. Parker

Table 3

CLAY MINERALOGY

Sample	Percentage of Clay Fraction*					
	Kaolinite	Quartz	Illite-Mica	Chlorite-Montmorillonite	Amorphous	Feldspar
Parker Soil A	14	-	35	51	-	-
B	14	-	39	47	-	-
Kosse Kaoline	85	10	5	-	-	-
Ranger Shale	24	28	24	10	9	5
Fire Clay	78	16	6	-	-	-

*Values represent fraction of the clay portion of the sample. Parker Soil was 10.5 percent clay; Kosse Kaoline ∿ 53 percent; Ranger Shale, 40 percent; and Fire Clay, 44 percent. (See Table 2). No deflocculant used.

A and B are duplicates.

Dash (-) indicates negligible amounts found.

Figure 7. Moisture-Density Relationship for Kosse Kaoline

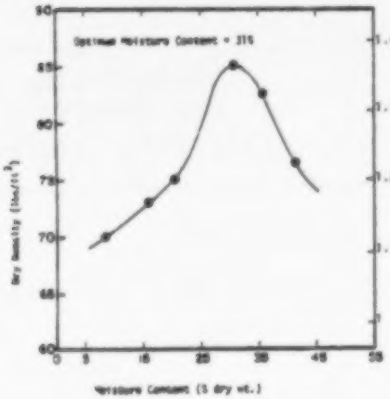

Figure 8. Moisture-Density Relationship for Ranger Shale

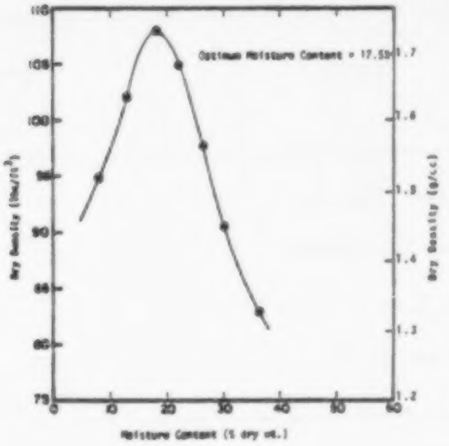

Figure 9. Moisture-Density Relationship for Fire Clay

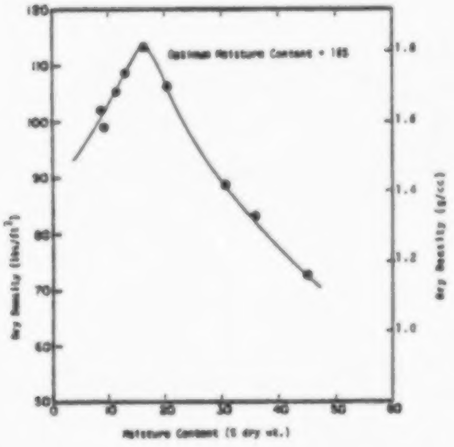

Figure 10. Moisture-Density Relationship for Parker Soil

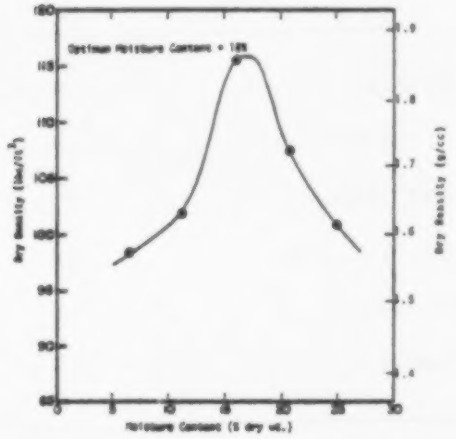

Table 4

OPTIMUM MOISTURE CONTENTS

Sample	Optimum Moisture Content (%)	Corresponding Dry Density (lbs/ft^3)	(g/cc)
Ranger Shale	17.5	108	1.73
Kosse Kaoline	31	85	1.36
Fire Clay	16	113	1.81
Parker Soil	18	116	1.86

Table 5

ATTERBERG LIMITS

Sample	Plastic Limit Moisture (%)	Liquid Limit Moisture (%)	Plasticity Index Moisture (%)
Ranger Shale	36	46	10
Kosse Kaoline	38	50	12
Fire Clay	31	32	1
Parker Soil	22	26	4

Soil had the greatest dry density at optimum moisture content, followed by Fire Clay, Ranger Shale and Kosse Kaoline.

For a given soil sample, the maximum dry density represents the minimum void ratio. That is, at maximum dry density the ratio of the volume of voids to the volume of solid material is a minimum. At maximum dry density, the porosity of a given material is, therefore, at its lowest point. The dry densities reported here are somewhat higher than those determined by Sanks et al. (1975) who measured values ranging from 60 to 95 lb/ft^3 (0.96 to 1.52 g/cc) for six different Texas soils. The moisture content and dry density were used to calculate the void ratio. (See discussion of Permeability.)

Atterberg Limits

The values for the Atterberg Limits for the solid substrates are presented in Table 5. The plastic and liquid limits were in the order Kosse Kaoline > Ranger Shale > Fire Clay > Parker Soil and the plasticity index followed the order Kosse Kaoline > Ranger Shale > Parker Soil > Fire Clay.

Mitchell (1976, p. 173) has collected data on Atterberg Limits for various clays and these indicate that montmorillonite has the highest liquid and plastic limits (100 to 900 percent and 50 to 100 percent, respectively) followed by illite (60 to 120 percent and 35 to 60 percent) and kaolinite (30 to 110 percent and 25 to 40 percent). These data are for various ionic forms and the ranges of values reflect the dependency of soil plasticity on the type of substituted cation. The Atterberg Limits obtained in this study are quite low when compared with the ranges given by Mitchell for pure clays. This is probably due to the high percentage of silt in the samples evaluated in this study.

Odell et al. (1960) have shown that the Atterberg Limits can be correlated with the percent clay in a soil and have presented equations relating liquid and plastic limits and plasticity index to the percentage of particles less than 0.002 mm (clay). In general, liquid limits observed in this study were smaller than those estimated on the basis of Odell et al.'s equations, while observed plastic limits were larger. The measured plasticity indices are thus considerably lower than predicted. Other factors besides percentage clay, such as percent organic carbon and percent montmorillonite clay also influence plasticity and these could in part be responsible for the observed differences.

Seed et al. (1964) have related the plasticity index to the tendency of a clay to undergo swelling. In general, the higher the plasticity index, the greater the total expansion of the clay when exposed to water. The plasticity indices determined in this study suggest that Ranger Shale and Kosse Kaoline should expand more than Fire Clay. This trend was observed in this study and is commented on in a later section of this report. (See section on Swelling.)

Cation Exchange Capacity

The cation exchange capacities (CEC) of the solid substrates examined are presented in Table 6. The Kosse Kaoline, Fire Clay, and Parker Soil had CEC values ranging from 11 to 14 meq/100 g, whereas the value for the Ranger Shale was about 54 meq/100 g. The CEC of montmorillonite typically ranges from 80 to 150 meq/100 g as compared with 3 to 5 meq/100 g and 10 to 40 meq/100 g values for kaolinite and illite, respectively (Grim, 1953). The low CEC values obtained are in keeping with the generally low montmorillonite content of these clays.

TABLE 6. CATION EXCHANGE CAPACITY

Sample	Cation Exchange Capacity(CEC) (meq/100 g) Test No. 1	Test No. 2	Average
Kosse Kaoline	13.4	13.3	13.4
Fire Clay	11.2	11.2	11.2
Ranger Shale	54.8	54.0	54.4
Parker Soil	13.4	14.8	14.1

Cation exchange capacity might be expected to have a marked effect on the capacity of a soil to attenuate the movement of heavy metals from a landfill to groundwater supplies. The effect of CEC on the movement of apolar organic solvents has not been investigated.

Exchangeable Cations

Ranger Shale, Kosse Kaoline and Fire Clay were examined for exchangeable Na, K, Ca and Mg. The results which are presented in Table 6A, indicate that for all these clay-soils, calcium was the dominant exchangeable cation. Na and K were present in relatively small amounts and magnesium could not be detected in any of the samples. Ranger Shale, which had the highest CEC also had the largest amount of exchangeable calcium.

TABLE 6A. EXCHANGEABLE Na, K, Ca, AND Mg
(meq/100 g)

Sample	Ca	Mg	Na	K
Fire Clay	9.7	-	0.5	0.3
Kosse Kaoline	4.6	-	2.0	0.3
Ranger Shale	59	-	1.0	0.7

Dash (-) indicates none detectable.

Major Ions

The three clay-soils used most frequently in tests with organic solvents in this study, namely Ranger Shale, Kosse Kaoline, and Fire Clay, were analyzed for major elements using the Applied Research Laboratory Electron Microprobe. Five of the major elements in each clay were determined using the electron microprobe and their values are expressed in weight percent of oxide in Table 7. As expected, in all clays used, the dominant cation determined was Si and the second most dominant was Al.

The relatively high percentage of potassium in Ranger Shale was a reflection of its substantial illite content, illite being a clay-sized muscovite ($K_2Al_4(Si_6Al_2)O_2(OH)_4$), or a muscovite-montmorillonite mixture. The iron present in the Ranger Shale probably substituted for aluminum in the aluminum-hydroxyl unit, as in the mineral nontronite.

Kosse Kaoline was the richest in calcium while Fire Clay was characterized by a high aluminum content. There are no apparent correlations between major ion content and other properties reported herein.

Total Carbon and Carbonate Content

The percent total carbon and percent carbonate content of the test soils are presented in Table 8. All four test samples contained low percentages of both total carbon and carbonate with the Ranger Shale, Kosse Kaoline and Fire Clay containing less than one percent total carbon. The Parker soil contained approximately three percent total carbon. The carbonate content ranged from zero in the Kosse Kaoline and Fire Clay to approximately 0.4 percent in the Parker soil. The higher carbonate content in the Parker soil is to be expected since it is from a calcareous area containing large amounts of detrital limestone.

Lee and Jones (1978) have commented on the ability of organic carbon to increase the sorptive capacity of soils for certain types of organic pollutants. It also appears to be the case (see section on Swelling) that clays having a high organic carbon content swell more extensively in organic (waste) liquids than clays with a low organic content. The significance of this is discussed in a later section.

TABLE 7. MAJOR ION CONTENT OF CLAYS STUDIED
(all values in weight percent of oxide)

Clay	Fe_2O_3	K_2O	Al_2O_3	CaO	SiO_2	Total
Ranger Shale	6.10	2.35	15.13	3.11	42.88	69.57
Kosse Kaoline	0.34	0.21	27.4	9.36	41.28	78.59
Fire Clay	1.37	0.74	35.29	4.03	50.67	92.10

TABLE 8. TOTAL CARBON AND CARBONATE CONTENT

Sample		% Total Carbon	% Carbonate
Ranger Shale	A	0.61	0.32
	B	0.60	0.33
	Average	0.60	0.32
Kosse Kaoline	A	0.11	0
	B	0.12	0
	Average	0.12	0
Fire Clay	A	0.03	0
	B	0.03	0
	Average	0.03	0
Parker Soil	A	3.16	0.41
	B	3.19	0.42
	Average	3.18	0.42

A and B are duplicate tests

EFFECTS OF ORGANIC SOLVENTS ON CLAY LATTICE SPACING

X-ray diffraction data were collected for the clay-soils which had been in contact with solvents and with solvent mixtures. Values of 2θ were converted to lattice spacings by using the Bragg relationship. All data for pure solvents are presented in Tables 9 through 12. The purpose of this part of the investigation was to examine the effect of solvents on clay lattice spacings in order to determine whether or not a correlation could be found between lattice spacing and permeability. The existence of such a correlation would enable permeabilities to be predicted from easily-obtained X-ray diffraction measurements.

Initial work focused on the effect of water, acetone, carbon tetrachloride, xylene, trichloroethylene (TCE) and aqueous mixtures of these organic solvents on Ranger Shale. Data for the neat liquids are presented in Table 9. Examination of these values indicates that there is little, if any, relationship between the lattice spacing and solvent type. The d(001) values ranged from 13.95 Å for TCE to 14.34 Å for acetone, with no obvious correlation between the spacings and molecular properties. Furthermore, the spacings were all sufficiently close to the d(001) value for Ranger Shale in contact with water that, given the errors to be expected in these measurements (± 0.2 to 0.3 Å), it was concluded that what was being observed was the spacing for the Ranger Shale-water interlayer complex. This indicates that in the presence of atmospheric moisture, or in the presence of even the small amounts of water dissolved in the nominally pure organic liquids, Ranger Shale will preferentially form a characteristic water complex with possibly complete exclusion of the organics from the interlayer region. The data in Table 13 show that this is true for the mixtures as well. (It should be pointed out here that the mixtures are, with the exception of acetone-water, two-phase systems where the aqueous phase is saturated with organic component and the organic phase is saturated with water. Solvent systems of this type would be in contact with clay in a typical disposal pit). This behavior can be explained if intercalation is recognized to be a competitive process wherein molecules in the treatment solution compete for sites around the interlayer cation. Water, because it is a small, highly polar molecule, can effectively out-compete any of the organics studied here for solvation sites in the clay, even when it is present in relatively minute amounts.

Barshad (1952) discussed the problems involved in forming characteristic clay-organic complexes and showed that for a number of weakly polar molecules, such a complex can only be formed, if at all, by dehydration of the clay at temperatures up to 250°C. Benzene, even under the extreme conditions used by Barshad, gave no complex. Olejnik et al. (1974) in their study of the montmorillonite swelling in polar liquids, found it necessary to pretreat the clay by heating at 150°C and 4×10^{-4} mm of mercury to remove traces of water. They also took care to scrupulously dry the immersion liquid over a molecular sieve for several days.

TABLE 9. RESULTS OF X-RAY DIFFRATION MEASUREMENTS OF AIR DRIED RANGER SHALE AFTER EXPOSURE TO VARIOUS SOLVENTS

Solvent		Values of 2θ							Calculated Values of d(Å)						
		1st	2nd	3rd	4th	5th	6th	7th	1st	2nd	3rd	4th	5th	6th	7th
Acetone	A	6.2	8.8	12.4	17.8	20.9	24.9	26.7	14.3	10.0	7.1	5.0	4.3	3.6	3.3
	B	-	8.7	12.3	17.7	20.9	24.8	26.6	-	10.2	7.2	5.0	4.3	3.6	3.3
Xylene	A	6.3	8.8	12.5	17.8	21.0	25.0	26.7	14.0	10.0	7.1	5.0	4.2	3.6	3.3
	B	6.2	8.9	12.4	17.8	20.9	24.9	26.7	14.1	9.9	7.1	5.0	4.2	3.6	3.3
Carbon Tetrachloride	A	6.3	8.8	12.4	17.8	20.9	25.0	26.7	14.0	10.0	7.1	5.0	4.2	3.6	3.3
	B	6.2	8.8	12.3	17.7	20.8	24.9	26.6	14.2	10.0	7.2	5.0	4.3	3.6	3.3
Trichloro-ethylene	A	6.3	8.9	12.4	17.8	21.0	24.5	26.7	14.1	10.0	7.1	5.0	4.2	3.6	3.3
	B	6.4	8.9	12.4	17.8	20.8	25.0	26.7	13.8	10.0	7.1	5.0	4.3	3.6	3.3
Water*	A	6.1	8.8	12.4	17.8	20.9	25.0	26.7	14.4	10.0	7.1	5.0	4.3	3.6	3.3
	B	6.2	8.8	12.4	17.8	20.9	24.9	26.6	14.4	10.0	7.1	5.0	4.3	3.6	3.3
	A	6.3	-	-	-	-	-	-	14.1	-	-	-	-	-	-
	B	6.2	-	-	-	-	-	-	14.2	-	-	-	-	-	-
	A	6.2	-	-	-	-	-	-	14.2	-	-	-	-	-	-
	B	6.2	-	-	-	-	-	-	14.3	-	-	-	-	-	-

A and B are replicate samples.

*3 sets of duplicates run.

Dash (-) indicates not measured.

TABLE 10. RESULTS OF X-RAY DIFFRACTION MEASUREMENTS FOR AIR-DRIED KOSSE KAOLINE IN CONTACT WITH VARIOUS SOLVENTS

Solvent		Values of 2θ							Calculated Values of d(Å)						
		1st	2nd	3rd	4th	5th	6th	7th	1st	2nd	3rd	4th	5th	6th	7th
Acetone	A	5.6	8.9	12.4	17.8	22.6	25.0	26.7	15.8	9.9	7.1	5.0	3.9	3.6	3.3
	B	5.6	8.9	12.4	17.8	22.5	25.0	26.8	15.7	9.9	7.1	5.0	3.9	3.6	3.3
Benzene	A	5.2	8.9	12.4	17.9	22.6	25.0	26.8	17.0	9.9	7.1	5.0	3.9	3.6	3.3
	B	5.1	8.8	12.4	17.9	22.6	25.0	26.7	17.3	10.0	7.2	5.0	3.9	3.6	3.3
Xylene	A	5.4	8.8	12.4	17.8	22.6	25.0	26.7	16.5	10.0	7.1	5.0	3.9	3.6	3.3
	B	5.4	8.8	12.4	17.7	22.5	25.0	26.8	16.2	10.0	7.1	5.0	3.9	3.6	3.3
Carbon Tetrachloride	A	5.6	8.8	12.4	17.8	22.6	25.0	26.8	15.7	10.0	7.1	5.0	3.9	3.6	3.3
	B	5.6	8.8	12.4	17.8	22.5	25.0	26.7	15.9	10.0	7.2	5.0	4.0	3.6	3.3
Trichloro-ethylene	A	5.5	8.9	12.4	17.8	22.5	25.0	26.7	16.0	9.9	7.2	5.0	3.9	3.6	3.3
	B	5.6	8.8	12.5	17.7	22.5	25.0	26.7	15.8	10.0	7.1	5.0	3.9	3.6	3.3
Water	A	5.3	8.8	12.4	17.8	22.6	25.0	26.9	16.8	10.0	7.1	5.0	3.9	3.6	3.3
	B	5.1	8.9	12.4	17.8	22.5	25.0	26.9	17.3	9.9	7.1	5.0	3.9	3.6	3.3

A and B are replicate Samples.

TABLE 11. RESULTS OF X-RAY DIFFRACTION MEASUREMENTS FOR AIR-DRIED FIRE CLAY IN CONTACT WITH VARIOUS SOLVENTS

Solvent		Values of 2θ							Calculated Values of $d(\mathring{A})$						
		1st	2nd	3rd	4th	5th	6th	7th	1st	2nd	3rd	4th	5th	6th	7th
Acetone	A	5.6	8.9	12.2	17.7	22.7	24.9	26.7	15.8	9.9	7.2	5.0	3.9	3.6	3.3
	B	5.4	8.8	12.2	17.7	22.5	25.0	26.6	16.4	10.1	7.2	5.0	3.9	3.6	3.3
Benzene	A	5.2	8.9	12.2	17.8	22.4	25.0	26.7	17.0	9.9	7.2	5.0	4.0	3.6	3.3
	B	5.2	8.5	12.1	17.7	22.4	24.7	26.5	16.9	10.4	7.3	5.0	4.0	3.6	3.4
Xylene	A	5.0	8.9	12.3	17.7	22.5	25.0	26.7	17.8	10.0	7.2	5.0	3.9	3.6	3.3
	B	5.3	9.0	12.2	17.7	22.6	24.9	26.8	16.6	9.8	7.2	5.0	3.9	3.6	3.3
Carbon Tetrachloride	A	5.5	8.9	12.2	17.9	22.5	25.0	26.7	16.1	9.9	7.2	5.0	3.9	3.6	3.3
	B	5.4	8.8	12.3	17.9	22.5	24.9	26.6	16.4	10.1	7.2	5.0	3.9	3.6	3.3
Trichloro-ethylene	A	5.5	8.8	12.3	17.8	22.4	25.0	26.7	16.1	10.0	7.2	5.0	4.0	3.6	3.3
	B	5.5	8.7	12.2	17.6	22.3	24.9	26.6	16.1	10.2	7.3	5.0	4.0	3.6	3.4
Water	A	5.6	8.9	12.5	17.9	22.8	25.2	27.0	15.8	10.0	7.1	5.0	3.9	3.5	3.3
	B	5.4	8.8	12.3	17.8	22.5	25.0	26.8	16.3	10.1	7.2	5.0	3.9	3.6	3.3

A and B are replicate samples.

TABLE 12. RESULTS OF X-RAY DIFFRACTION MEASUREMENTS FOR AIR-DRIED PARKER SOIL IN CONTACT WITH VARIOUS SOLVENTS

Solvent		Values of 2θ							Calculated Values of d(Å)						
		1st	2nd	3rd	4th	5th	6th	7th	1st	2nd	3rd	4th	5th	6th	7th
Acetone	A	6.5	8.7	12.6	17.0	23.1	26.7	29.4	13.6	10.1	7.0	5.2	3.8	3.3	3.0
	B	6.3	8.9	12.0	16.8	23.1	26.7	29.5	14.0	9.9	7.4	5.3	3.8	3.3	3.0
Benzene	A	6.3	8.3	12.5	16.9	23.0	26.7	29.4	14.0	10.7	7.1	5.3	3.9	3.3	3.0
	B	6.2	8.3	12.4	16.9	23.1	26.7	29.5	14.2	10.7	7.1	5.2	3.8	3.3	3.0
Xylene	A	6.4	8.4	12.9	16.6	23.1	26.8	29.5	13.8	10.5	6.9	5.3	3.8	3.3	3.0
	B	6.4	8.5	12.5	16.3	23.0	26.6	29.4	13.8	10.4	7.1	5.4	3.9	3.9	3.0
Carbon Tetrachloride	A	7.0	8.8	12.2	16.9	23.0	26.6	29.4	12.6	10.0	7.3	5.2	3.9	3.9	3.0
	B	6.2	9.1	12.2	16.5	23.1	26.7	29.5	14.3	9.7	7.2	5.4	3.8	3.3	3.0
Trichloroethylene	A	7.6	8.5	12.4	16.5	23.1	26.7	29.4	11.6	10.4	7.2	5.4	3.9	3.3	3.0
	B	7.6	8.5	12.4	16.4	23.1	26.6	29.5	11.6	10.4	7.1	5.4	3.8	3.3	3.0
Water	A	6.4	8.1	12.1	16.6	23.2	26.8	29.5	13.8	11.0	7.3	5.3	3.8	3.3	3.0
	B	6.6	8.8	12.3	16.2	23.1	26.7	29.5	13.3	10.0	7.2	5.5	3.8	3.3	3.0

A and B are replicate samples.

TABLE 13. RESULTS OF X-RAY DIFFRACTION MEASUREMENTS OF AIR DRIED MONTMORILLONITE AFTER EXPOSURE TO VARIOUS SOLVENT-WATER MIXTURES

Treatment Solution (Volume % Organic)		Mean Value of d (Å)		
		1st	2nd	3rd
0% Acetone		14.36	10.04	7.13
5		14.44	10.00	7.15
25		14.48	10.04	7.16
50		14.38	10.10	7.19
75		14.60	10.21	7.19
100		14.34	10.10	7.15
0% Carbon Tetrachloride	(14.23)*	14.26	10.00	7.14
5		14.13	9.95	7.12
25	(14.03)	14.15	9.94	7.13
50	(14.22)	14.21	9.96	7.13
100		14.12	10.02	7.13
5% Xylene	(14.31)	13.88	9.94	7.12
25	(14.04)	14.02	9.96	7.10
50	(14.23)	14.13	9.97	7.12
100		14.08	9.96	7.13
5% Trichloroethylene		14.13	9.96	7.13
25		14.26	10.03	7.12
50		13.94	10.02	7.12
100		13.95	9.94	7.13

* Values for 1st d(Å) for additional run.

Since this study centers on how clays behave when in contact with organic solvents under conditions approximating those in the field, such measures as dehydrating the clay and the immersion liquid were considered unnecessary and indeed, inappropriate.

From the work with Ranger Shale, it appears that when an organic liquid containing small quantities of moisture (as would be the case in the field) is in contact with air-dried clay, the lattice spacing (d(001)) will be that corresponding to the clay-water complex (∿14.2Å) regardless of the organic solvent involved. That is, there is no penetration of organic molecules into the inter-layer spaces.

After the study of Ranger Shale, it was decided that only pure solvents should be looked at since mixtures appeared to yield little interpretable information. Samples of Kosse Kaoline, Fire Clay and Parker Soil in contact with six solvents were X-rayed and the d(001) values were computed. These are summarized in Table 14. Similarities in lattice spacings regardless of solvent were again apparent. For example, the d(001) value for Kosse Kaoline in acetone, xylene, CCl_4 and TCE were all in the vicinity of 16 Å. The similarity of effects of water and benzene, two highly dissimilar solvents, appeared to be anomalous. Values for Fire Clay in acetone, CCl_4, TCE and water are also about 16 Å, with benzene and xylene being slightly greater. For Parker Soil, d(001) values were all close to 14 Å with the exception of TCE which gave a spacing a full 2.5 Å lower.

A rationale has been presented for the constancy of the lattice spacing for Ranger Shale in a variety of solvents running the gamut of molecular properties. The same explanation applies to the other clays. The exceptions noted above are more difficult to account for and no attempt will be made to do so in this report.

TABLE 14. d(001) SPACING FOR CLAYS IN CONTACT WITH PURE SOLVENTS

Clay / Solvent	Fire Clay	Kosse Kaoline	Ranger Shale	Parker Soil
Acetone	16.08	15.78	14.34	13.79
Benzene	16.96	17.16	-	14.07
Xylene	17.18	16.36	14.03	13.79
CCl_4	16.26	15.78	14.12	14.26
TCE	16.09	15.89	13.96	11.62
Water	16.07	17.07	14.26	13.57

Dash (-) indicates not measured; see previous discussion in Methods Section.

SORPTION ISOTHERM STUDIES

In waste disposal areas, sorption onto the native soil or clay liners is one of the most important mechanisms relied upon for preventing the movement of hazardous materials from the disposal area to groundwater. This characteristic is crucial in explaining and predicting the permeability of a soil or clay to water and organic solvents.

Transport of contaminants is primarily determined by the permeability of the material through which this solution is passing. As previously discussed, the permeability of clays could be markedly affected by organic solvents. However, even if the clays are sufficiently permeable to allow transport of the liquid consisting of a water-organic mixture, the organic is only of consequence in affecting groundwater quality if the clay sorption capacity for that organic is exceeded. Therefore, it becomes important to learn something about the extent of sorption of organics on clays. This is an area that has received attention in this study.

Tables 15,16, and 17 present the data collected for the sorption of various organic compounds on Ranger Shale, Kosse Kaoline, and Fire Clay. These data were used to define the Freundlich isotherms according to: (Glasstone, 1955)

$$\log(x/m) = (\log K) + ((1/n)\log C_e) \qquad (34)$$

where x = amount sorbed in millimoles,
m = mass of clay in kg, and
C_e = equilibrium concentration of the solute in millimole/l.
K and n = empirical constants

The ordinate, x/m, was calculated as follows:

$$x/m = ((C_i - C_e)V)/m \qquad (35)$$

where C_i = initial concentration in millimole/l and
V = volume of solution in contact with clay, in l.

The Freundlich isotherms for the organic solvents on the three clays are presented in Figures 11 through 20. Lines of best fit were determined visually. It appears that sorption in these organic-clay systems generally obeyed the Freundlich relationship as evidenced by the linear relationships seen in Figures 11 through 20. The Freundlich equation constants, K and n, were obtained from the plots and are reported in Table 18. The values of these constants are useful in estimating the amounts of sorption of the solvents on clays under various conditions and solute and clay concentration ranges.

TABLE 15. SORPTION OF ORGANIC SOLVENTS ON RANGER SHALE (25 ± 3°C)

Initial Conc. (mM)	Equilibrium Conc. (mMoles)	Wt. of Clay (grams)	Amount Sorbed (mMoles/kg)
	Benzene		
18.6	17.1	5.04	29.8
9.22	8.00	10.01	13.4
1.56	1.46	5.45	1.84
	m-xylene		
1.55	0.749	10.07	3.75
1.55	0.767	10.03	3.09
0.899	0.528	10.12	1.83
0.504	0.388	10.03	0.58
0.504	0.379	10.06	0.62
	Acetone		
39.16	37.07	25	8.36
15.94	14.75	25	4.76
3.87	3.06	25	3.24
	Carbon Tetrachloride		
9.09	5.50	20	14.36
3.08	1.83	20	5.00
2.29	1.60	20	2.76
2.29	1.40	20	3.56

TABLE 16. SORPTION OF ORGANIC SOLVENTS ON KOSSE KAOLINE (25 ± 3°C)

Initial Conc. (mM)	Equilibrium Conc. (mMoles)	Wt. of Clay (grams)	Amount Sorbed (mMoles/kg)
	Benzene		
18.6	15.3	5.03	65.6
9.28	8.68	1.65	36.3
1.56	1.53	1.02	2.94
1.56	1.46	5.03	1.99
	m-xylene		
1.00	0.875	1.08	28.9
1.00	0.812	2.13	22.1
1.00	0.688	6.03	12.9
1.00	0.638	8.02	11.3
1.00	0.559	15.09	7.3
	Carbon Tetrachloride		
4.92	1.23	3	43.0
4.92	1.39	4	29.1
4.92	1.39	5	21.9
4.92	1.33	6	17.4
4.92	1.12	12	6.33
4.92	0.88	15	4.04
4.92	0.66	18	2.60

TABLE 17. SORPTION OF ORGANIC SOLVENTS ON FIRE CLAY (25 ± 3°C)

Initial Conc. (mM)	Equilibrium Conc. (mMoles)	Wt. of Clay (grams)	Amount Sorbed (mMoles/kg)
	Benzene		
22.8	12.55	3	157.2
22.8	9.85	6	99.8
22.8	8.98	12	46.1
22.8	8.61	18	27.6
22.8	7.86	24	18.7
22.8	7.88	30	12.4
22.8	6.25	42	6.7
	m-xylene		
1.85	0.348	12	5.00
1.85	0.333	18	2.95
1.85	0.290	24	1.95
1.85	0.249	30	1.33
1.85	0.185	36	1.06
	Carbon Tetrachloride		
1.55	1.18	20	4.62
1.55	0.98	30	4.75
2.68	2.11	20	7.12
2.68	1.84	30	7.00
3.70	2.63	20	13.40
3.70	2.48	30	10.16
5.12	3.33	20	22.37
5.12	3.22	30	15.83

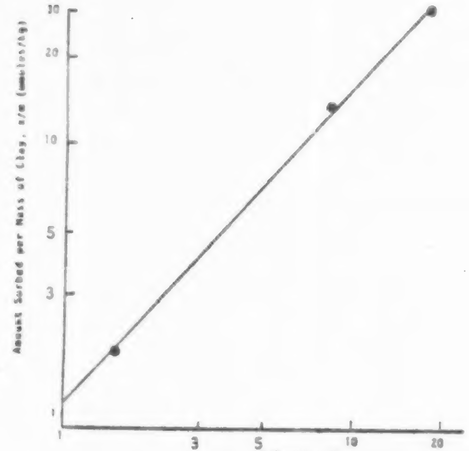

Figure 11. Freundlich isotherm for benzene sorption on Ranger Shale

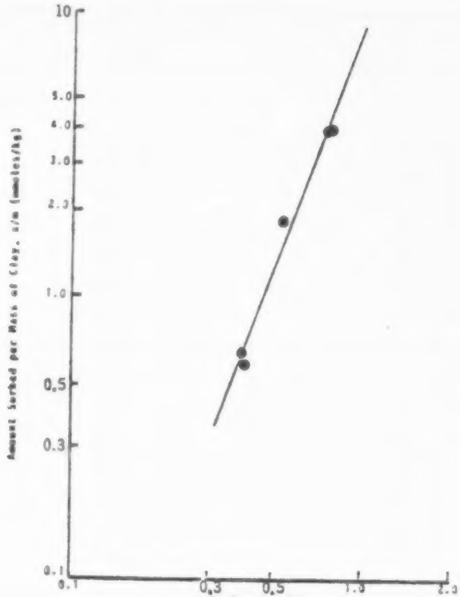

Figure 12. Freundlich isotherm for o-xylene sorption on Ranger Shale

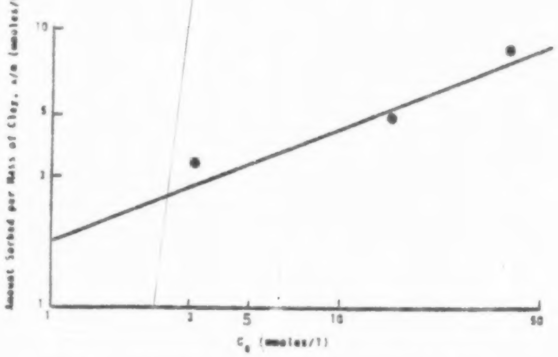

Figure 14. Freundlich isotherm for acetone sorption on Ranger Shale

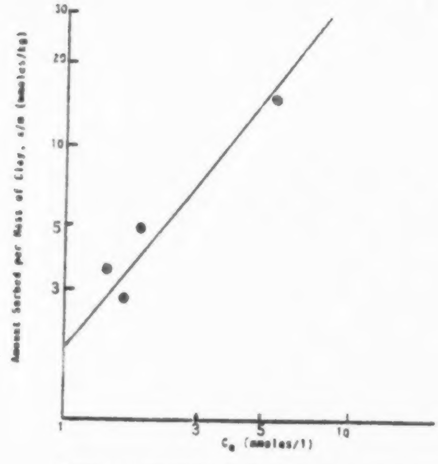

Figure 13. Freundlich isotherm for carbon tetrachloride sorption on Ranger Shale

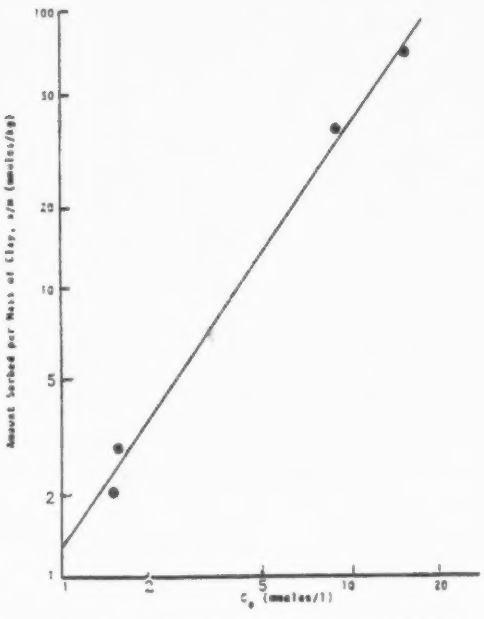

Figure 15. Freundlich isotherm for benzene sorption on Kosse Kaoline

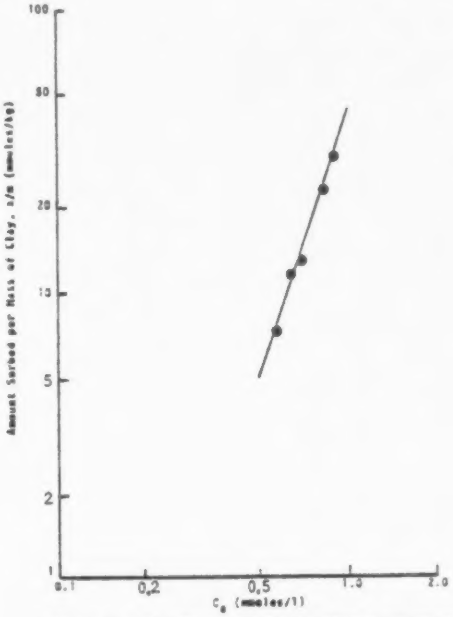

Figure 16. Freundlich isotherm for m-xylene sorption on Kosse Kaoline

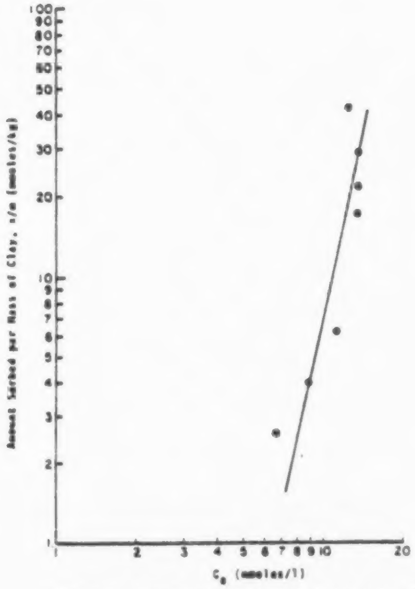

Figure 17. Freundlich isotherm for carbon tetrachloride sorption on Kosse Kaoline

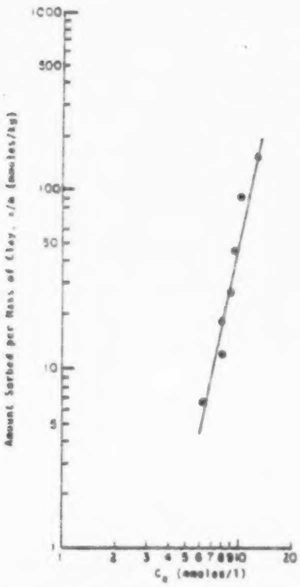

Figure 18. Freundlich isotherm for benzene sorption on Fire Clay

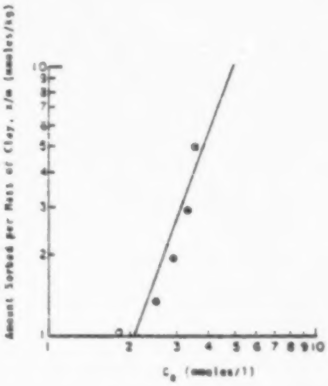

Figure 19. Freundlich isotherm for m-xylene sorption on Fire Clay

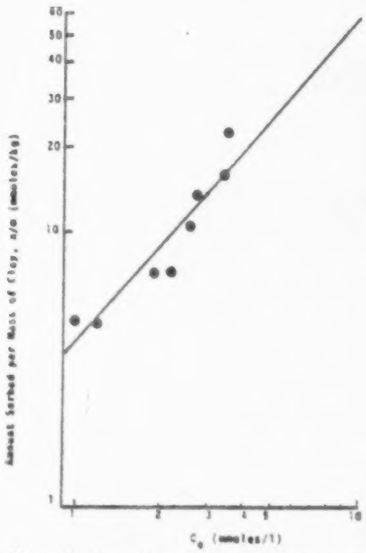

Figure 20. Freundlich isotherm for carbon tetrachloride sorption on Fire Clay

TABLE 18. FREUNDLICH EQUATION CONSTANTS FOR SORPTION OF ORGANIC SOLVENTS ONTO CLAYS

System	n	K
m-xylene/R.S.	0.36	7.5
CCl_4/R.S.	0.77	1.9
Benzene/R.S.	0.93	1.2
Acetone/R.S.	2.72	2.0
m-xylene/K.K.	0.34	42
CCl_4/K.K.	0.22	7.2
Benzene/K.K.	0.68	1.3
m-xylene/F.C.	0.36	72
CCl_4/F.C.	0.93	4.0
Benzene/F.C.	0.18	2.2×10^{-4}

R.S. = Ranger Shale
K.K. = Kosse Kaoline
F.C. = Fire Clay

One way the results of the sorption tests of the various solvents on the three clays can be compared is if the amount of organic sorbed is computed at a single equilibrium concentration. Comparable sorption values across solvents or sorbents can be obtained by extrapolation or interpolation of the x/m value which corresponds to an equilibrium concentration, C_e, of 1 millimolar. These x/m values for the systems tested are presented in Table 19.

These values can be interpreted in the following manner: If one kilogram of Kosse Kaoline, for example, is placed in an effectively infinite reservoir of a 1 mM aqueous solution of m-xylene, then the clay would sorb 42 millimoles of the organic compound. Examination of this table indicates that a greater amount of m-xylene tends to sorb per unit mass of clay than either CCl_4 or benzene. In general it appears that a greater amount of carbon tetrachloride than benzene would sorb onto clays. It is important to emphasize that these conclusions are based on the 1 mmolar equilibrium concentration of the solvent in contact with the clay and do not apply to substantially different concentration ranges. However, for Ranger Shale, where n increases from m-xylene through acetone, it can be supported using equation 34 that relative sorption is in the order m-xylene > CCl_4 > benzene > acetone for all equilibrium concentrations, C_e.

TABLE 19. SORPTION OF ORGANIC COMPOUNDS ONTO CLAYS AT EQUILIBRIUM CONCENTRATIONS OF 1 mM

(values in mmoles/kg)

Solute / Clay	Log Octanol/ Water Partition Coefficient*	Ranger Shale	Kosse Kaoline	Fire Clay
m- ylene	3.15	7.5	42	72
Carbon tetrachloride	2.64	1.9	7.2	4.0
Benzene	2.13	1.2	1.3	2.2x10^{-4}
Acetone	-0.24	2.0	-	-

Dash (-) indicates not measured.

*After Hansch et al. (1968).

The x/m value obtained for acetone at C_e=1 mM (2 mmoles/kg) falls within the range observed by Sanks et al. (1975) who found that acetone was sorbed by Texas clays to the extent of 0.8 to 10 mmoles/kg. They observed similar values for phenols. The extent of xylene uptake measured in the current study was considerably greater than the sorption of apolar DDT determined by Sanks et al. (1975). This is surprising since xylene is a more hydrophobic, less soluble substance than DDT and its sorption would be expected to have been less.

In light of the difficulties in determining sorption tendencies of highly volatile organics and in light of the goal of developing a model to predict the behavior of solvents and solvent mixtures based on more easily measured characteristics of the solvent(s) and the clays, it is of value to determine if the sorption tendency of a solvent can be related to one of its more readily measureable characteristics. Baughman and Lassiter (1978) suggested that the physical driving force for sorption of molecules from aqueous solution is the fugacity, or the escaping tendency of the solute from solution. One readily obtainable measure of the escaping tendency of a substance is its octanol/water partition coefficient, P, defined as the equilibrium concentration of a substance, i, in octanol, divided by its concentration in water when a small amount of i is equilibrated with an immiscible mixture of water and octanol, i.e.,

$$P = [C_i(oct)] / [C_i(H_2O)] \tag{36}$$

Thus, it might be expected that the greater the octanol/water partition coefficient, the greater the extent of sorption from aqueous solution onto a given clay-soil. The octanol/water partition coefficients for the organics tested are presented in Table 19. For Ranger Shale, Kosse Kaoline, and Fire Clay the order of sorption from the 1 millimolar solution paralleled the order of the log of the octanol/water partition coefficients, i.e., m-xylene, with the highest log P value, showed the greatest sorption, and benzene, with the lowest log P value, showed the least sorption at a C_e of 1 millimole/l. An exception was the sorption of acetone on Ranger Shale which was somewhat greater than for benzene at 1 mM. It would be expected, therefore, that substances such as m-xylene which have large P values or high escaping tendencies from aqueous solution would be taken up and immobilized by clays to a greater extent than benzene, for example, which has a smaller P value.

Based on the limited data collected it also appears that clay-soils having a high total weight percentage of kaolinite, such as Kosse Kaoline (45 percent) and Fire Clay (34 percent), have a larger sorptive capacity for apolar or weakly polar compounds than clay-soils with low kaolinite content such as Ranger Shale (9.6 percent). Based on these results it appears that soils rich in kaolinite will tend to reduce the concentration of hazardous, hydrophobic compounds in the aquatic environment to a greater degree than those clay-soils which are relatively poor in this mineral.

In the permeability section of this report it will be argued that the large and unexpected difference in the permeability of clay-soils to water on the one hand, and to several organic solvents covering a range of bulk and molecular properties on the other, is due to the ability of the clay-soils to strongly sorb and therefore to impede the motion of organic molecules through the column. It is at this juncture that the sorptive properties of clay-soils - organic systems becomes crucial in explaining and predicting the results of column tests and of field experiments.

As a final note on the sorption studies, it was observed that meta-xylene appeared to undergo isomeric conversion to para-xylene in the presence of Ranger Shale. A comparison of chromatograms for the m-xylene standard solution (Figure 21) and the same standard solution after 24 hours' contact with Ranger Shale (Figure 22) shows the appearance of a distinct new peak having the same retention time as p-xylene after exposure of the standard solution to Ranger Shale. When a solution containing a mixture of ortho, meta, and para isomers of xylene was left in contact with Ranger Shale for a three week period, the height of the peak associated with p-xylene increased relative to the others. Figure 23 is the chromatogram of the initial xylene solution; Figure 24

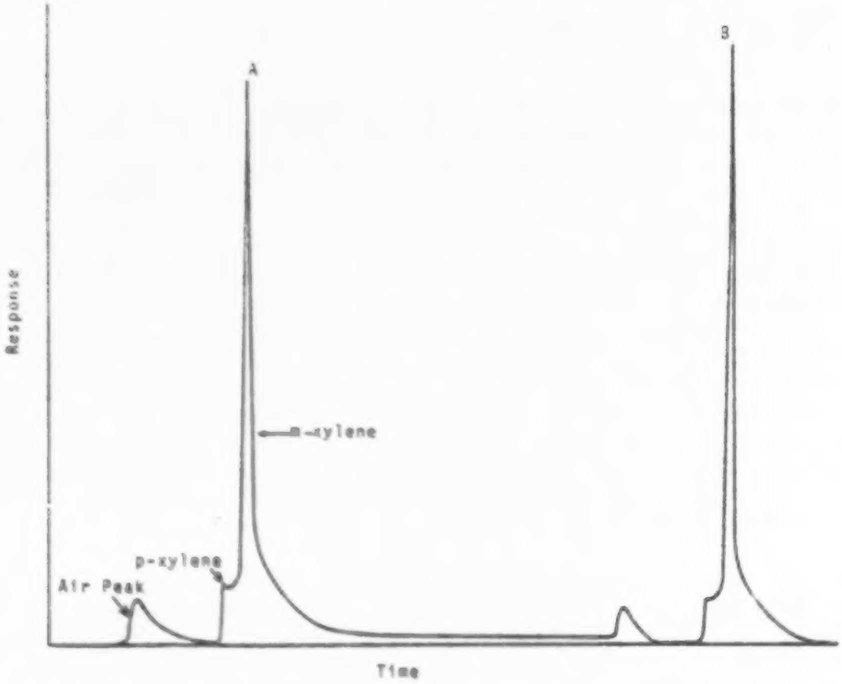

Figure 21. Chromatogram of m-xylene standard solution (A and B are duplicate injections)

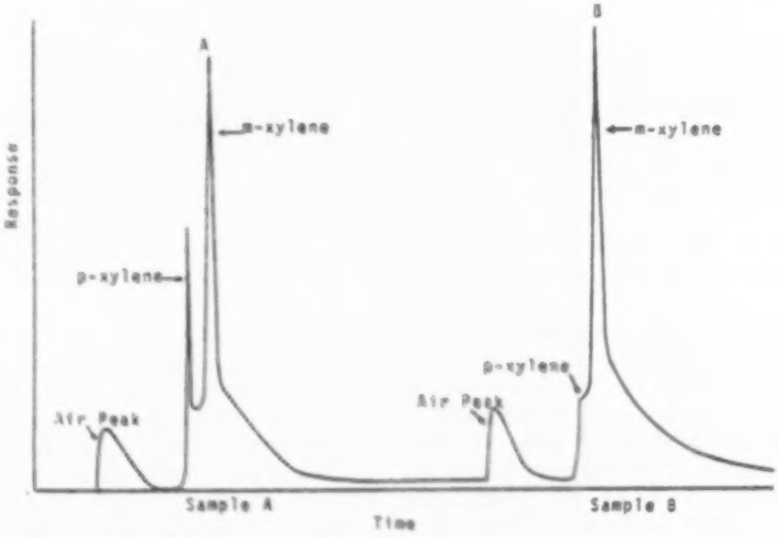

Figure 22. Chromatogram of m-xylene standard solution after 24-hr contact with Ranger Shale

Note: Samples A and B were taken from different bottles receiving the same treatment. Only A shows conversion.

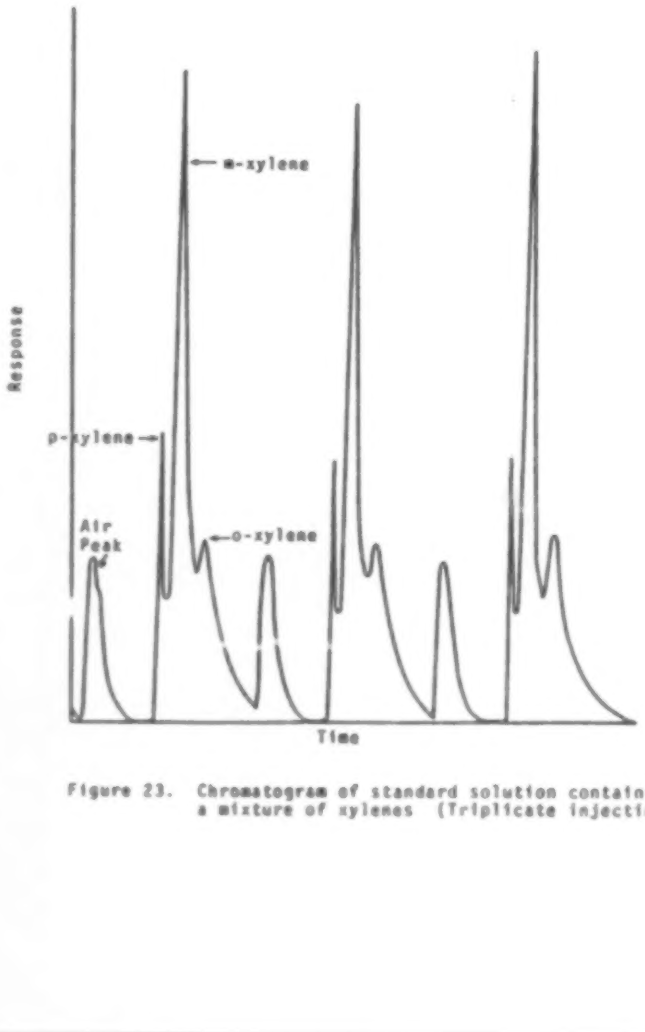

Figure 23. Chromatogram of standard solution containing a mixture of xylenes (Triplicate injections)

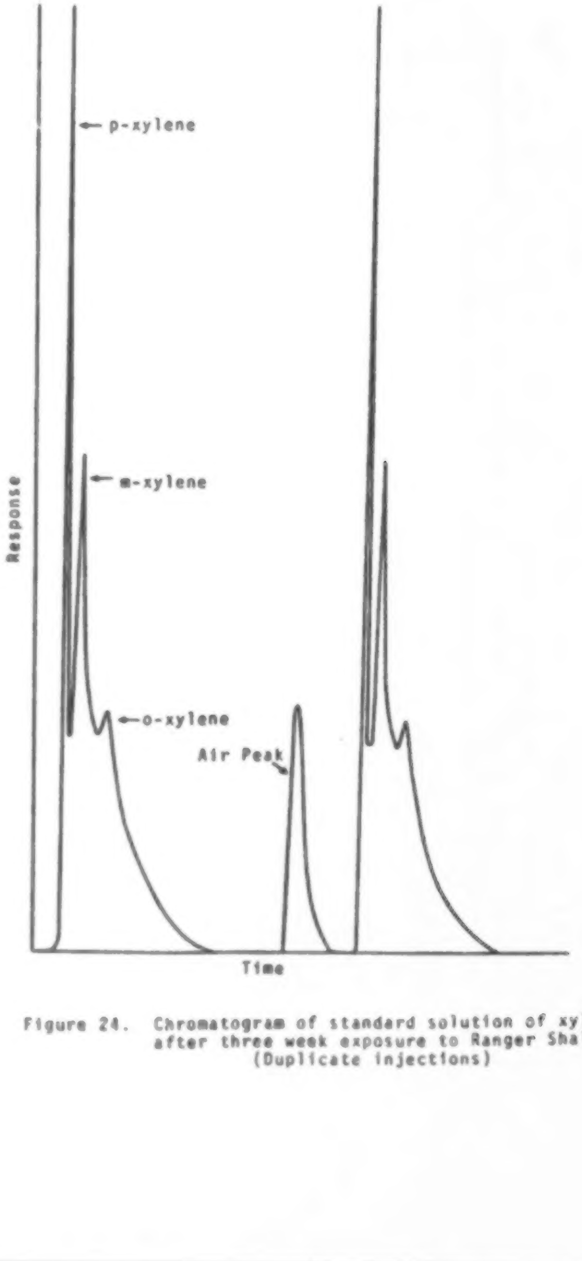

Figure 24. Chromatogram of standard solution of xylenes after three week exposure to Ranger Shale (Duplicate injections)

shows the increase in the height of the para-xylene peak after longer term exposure to Ranger Shale. This phenomenon was not investigated further, but it suggests that possible microbiological activity of the clay-soils might play a role in the transformation or decomposition of organic molecules in the environment, and might have a pronounced effect on parameters such as permeability (see permeability discussion).

SWELLING OF CLAYS IN CONTACT WITH WATER, ORGANIC SOLVENTS, AND SOLVENT MIXTURES

Another characteristic of clays which must be considered in evaluating the potential of a given system to transport organic solvent wastes is the solid's tendency to shrink or swell upon exposure to a liquid such as water and wastes disposed of on land. It is important then to determine the effect that organic solvents and solvent mixtures may have on this parameter. If a solvent causes an expandable layer clay to swell, this action could aid in waste retention; however, if it caused the lattice to shrink, additional transport of contaminants through a clay liner may result.

Results

Data on shrink and swell characteristics of the clays in contact with the various solvents and solvent mixtures examined are tabulated in Appendix Tables A 1 through A 25. The percent swell of the clays during contact with each solvent and solvent mixture tested is plotted as a function of time in Figures 25 through 48; smooth curves were fitted to the data visually.

Benzene caused the two clay-soils tested (Ranger Shale and Fire Clay) to shrink prior to causing them to swell (Figures 25 and 26). In the case of Ranger Shale, after shrinking by 0.07 percent, the clay swelled rapidly, reaching an equilibrium of about 0.05 percent swell after a total of about three days' exposure. For the Fire Clay exposed to benzene there was a three-day lag period prior to the shrinking (by 0.03 percent) during which swell to about 0.03 percent was noted. Overall, benzene caused the Fire Clay to swell to a greater degree than Ranger Shale; equilibrium at about 1.3 percent swell was reached after 28 days.

Xylene caused both Ranger Shale and Fire Clay to shrink (Figures 27 and 28). For both clays equilibrium was reached at about 28 days; maximum shrinkage of Ranger Shale was about 0.11 percent and of Fire Clay, about 0.25 percent. Xylene caused the Kosse Kaoline to swell 0.2 percent in about two days (Figure 29). The clay then appeared to gradually shrink by about 0.04 percent over the next 20 days of exposure.

Carbon tetrachloride caused Ranger Shale to swell after an approximately six day lag period (Figure 30). By the 14th day of exposure the clay had swelled by 1.1 percent where it remained for the duration of monitoring. The carbon tetrachloride caused both the Kosse Kaoline and Fire Clay to shrink (Figures 31 and 32). The Kosse Kaoline shrank by about 0.013 percent in the first day and maintained that level for about two weeks when the apparent equilibrium percent shrink increased to about 0.026 percent. Fire Clay showed a linear decrease in size until day 7 when it reached an equilibrium of about 0.63 percent shrink.

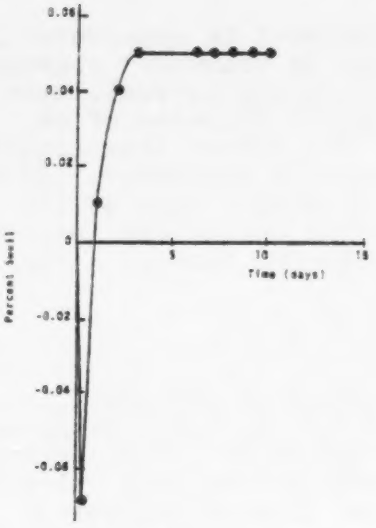

Figure 25. Swell properties for Ranger Shale in benzene
(See Table A1)

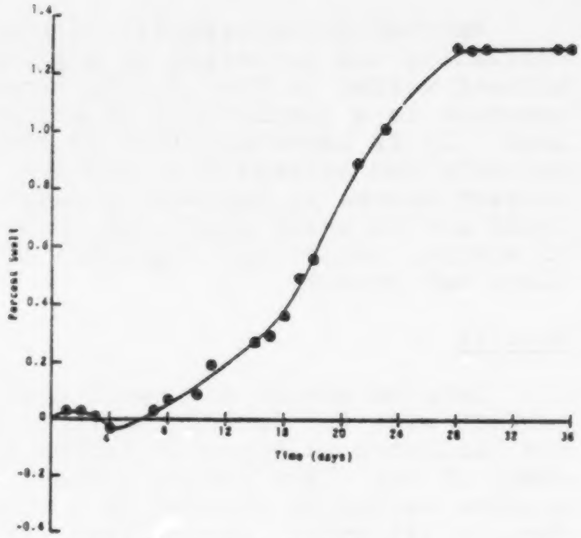

Figure 26. Swell properties for Fire Clay in benzene
(See Table A2)

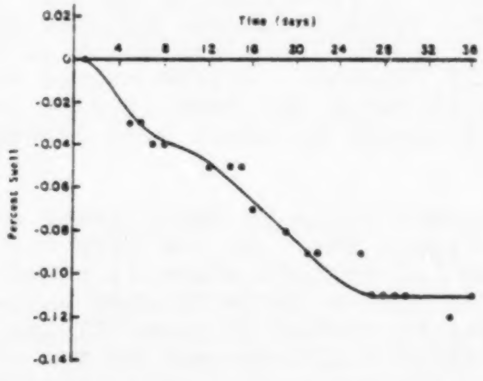

Figure 27. Swell properties for Ranger Shale in xylene
(See Table A3)

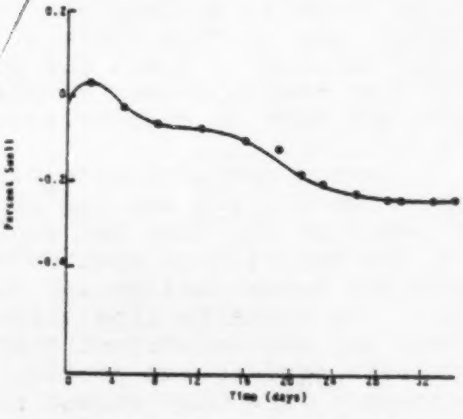

Figure 28. Swell properties for Fire Clay in xylene
(See Table A4)

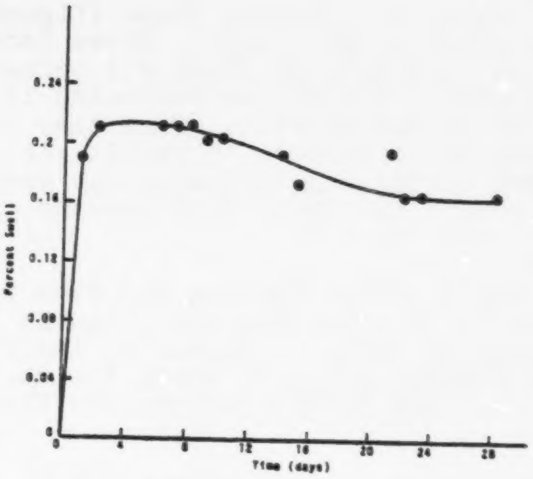

Figure 29. Swell properties for Kasse Kaoline in xylene.
(See Table A6)

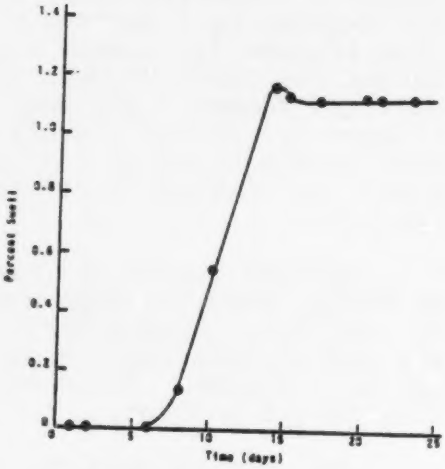

Figure 30. Swell properties for Ranger Shale in carbon tetrachloride
(See Table A6)

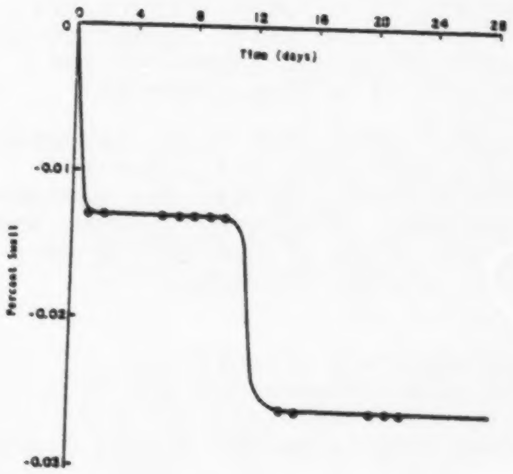

Figure 31. Swell properties for Kasse Kaoline in carbon tetrachloride
(See Table A7)

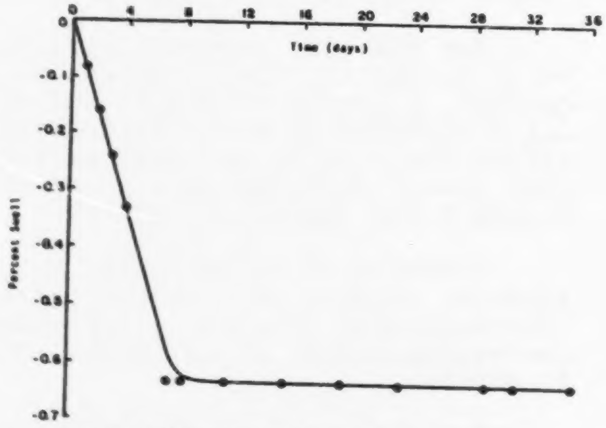

Figure 32. Swell properties for Fire Clay in carbon tetrachloride

Each of the three clay-soils exposed to trichloroethylene showed a different shrink-swell response. Ranger Shale (Figure 33) swelled by 1 percent over a several day period. Kosse Kaoline (Figure 34) showed a gradual shrinking by about 0.1 percent during the first 32 days of exposure. During the following 12 days, it showed a net swell of about 0.6 percent. Fire Clay (Figure 35) showed a swell of about 0.6 percent by day 2; the clay then shrank by about 0.53 percent during the following two weeks' exposure. Its net equilibrium result was about 0.07 percent swell.

Acetone caused the Ranger Shale, Kosse Kaoline and Fire Clay to swell, each reaching equilibrium in about one day (Figures 36, 37, and 38). Ranger Shale swelled by about 5 percent in the first day and equilibrated at about 4 percent swell by about the second day of exposure. Kosse Kaoline swelled by 8.5 percent and Fire Clay by 3.5 percent.

The last solvent tested on each clay was deionized water. For all clay-soils, it caused greater swelling than any of the other pure solvents tested. Duplicate swell measurements were made using Ranger Shale in deionized water. The data in Appendix Tables A16 and A17 show that in the first run, at equilibrium, the clay-soil had swelled by 11.55 percent and in the second run, by 11.83 percent. The rates of swell and swelling profiles (Figures 39 and 40) are the same within experimental error. The difference in the two values indicates that the relative error to be expected for these measurements is on the order of 2 percent. Kosse Kaoline in water also swelled by about 11 percent in about 5 days (Figure 41); Fire Clay swelled by about 8 percent in 12 days (Figure 42). For the same solvents tested, none of the three clays consistently showed greatest amount of swell; Ranger Shale and Kosse Kaoline tended to shrink to a greater extent than Fire Clay, however.

For the pure organic solvents tested with Fire Clay, benzene, acetone, and trichloroethylene caused a net swell (in order of decreasing amount of swell) and xylene and CCl_4 caused net shrinking. Exposure of Kosse Kaoline to acetone, trichloroethylene, and xylene resulted in net clay swelling (in order of decreasing percent swell) over the period monitored. Carbon tetrachloride caused Kosse Kaoline to shrink.

Exposure of Ranger Shale to pure methanol (Figure 43), glycerol (Figure 44), carbon tetrachloride (Figure 30) and trichloroethylene (Figure 33) resulted in clay swell (in order of decreasing amount of net swell) whereas xylene caused Ranger Shale to shrink.

Percent swell of Ranger Shale was tested using three acetone benzene mixtures; 25/75 mole % acetone/benzene (Figure 45); 50/50 mole % acetone/benzene (Figure 46); and 75/25 mole % acetone/benzene (Figure 47). In the 25/75 acetone/benzene solution Ranger Shale showed an initial shrinkage as was seen with

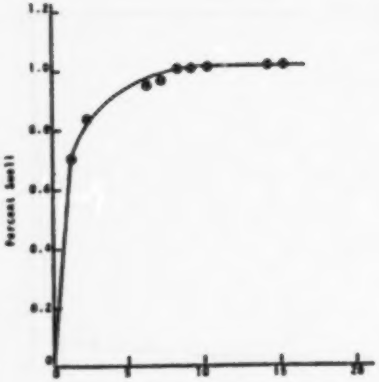

Figure 33. Swell properties for Ranger Shale in trichloroethylene

(See Table A9)

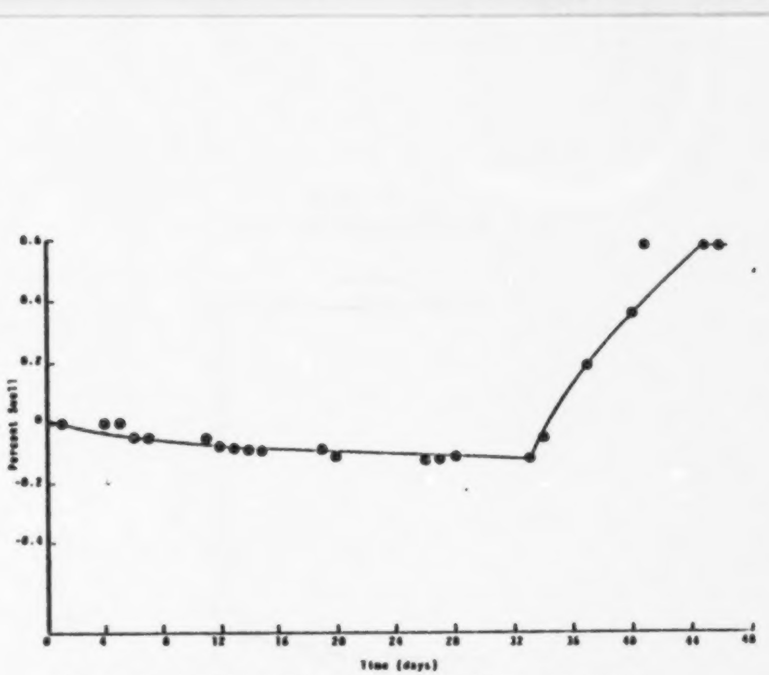

Figure 34. Swell properties for Kasse Kaoline in trichloroethylene. (See Table A10)

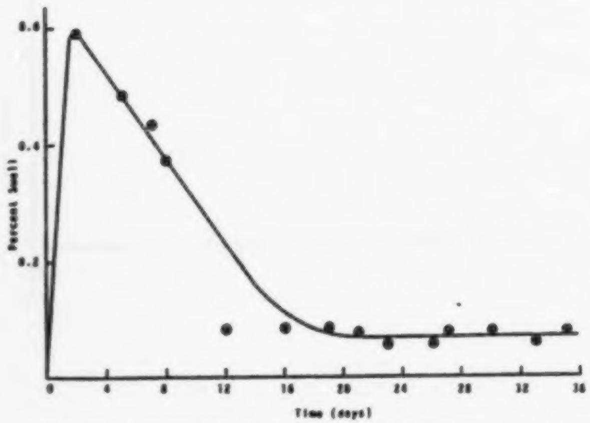

Figure 35. Swell properties for Fire Clay in trichloroethylene

(See Table A11)

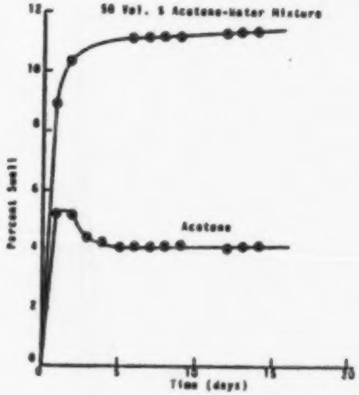

Figure 36. Swell properties for Ranger Shale in acetone and in 50 volume percent acetone-water mixture

(See Tables A12 and A13)

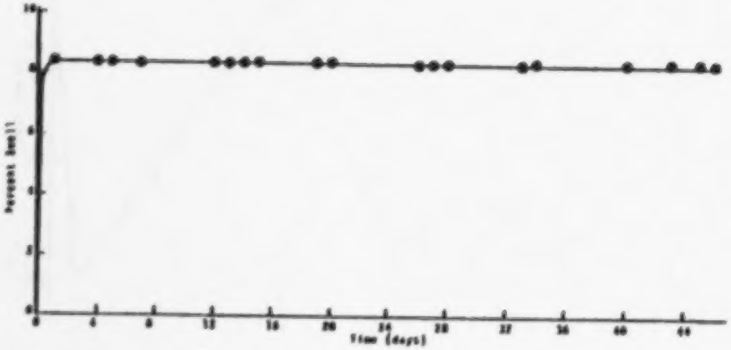

Figure 37. Swell properties for Kasse Kaolin
(See Table A14)

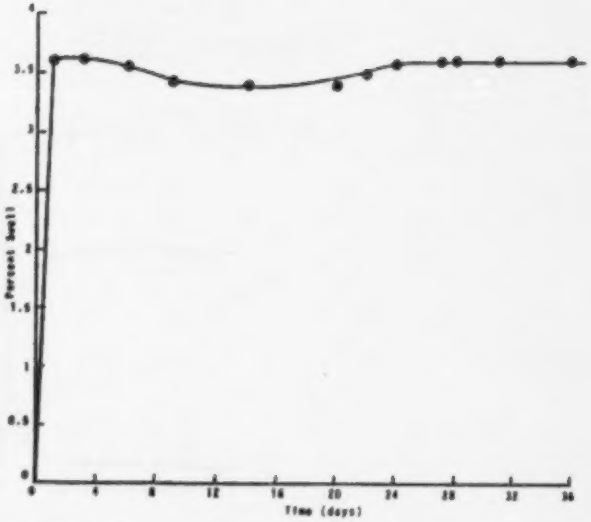

Figure 38. Swell properties for Fire Clay in acetone
(See Table A15)

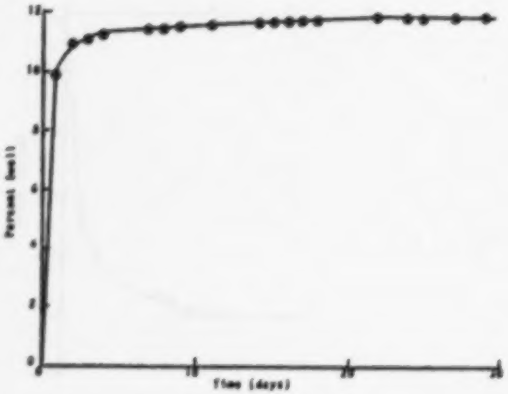

Figure 39. Swell properties for Ranger Shale in deionized water
(See Table A16)

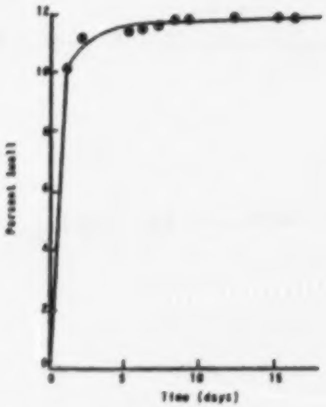

Figure 40. Swell properties for Ranger Shale in deionized water (duplicate)
(See Table A17)

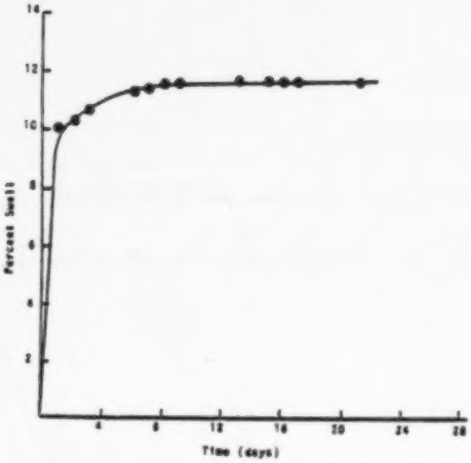

Figure 41. Swell properties for Kesse Kaoline in deionized water

(See Table A18)

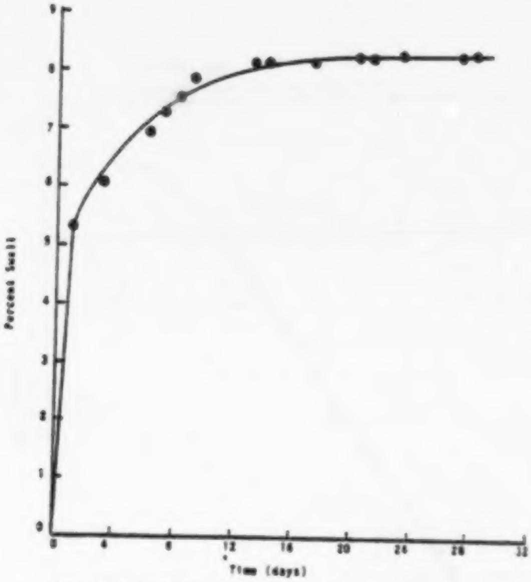

Figure 42. Swell properties for Fire Clay in deionized water

(See Table A19)

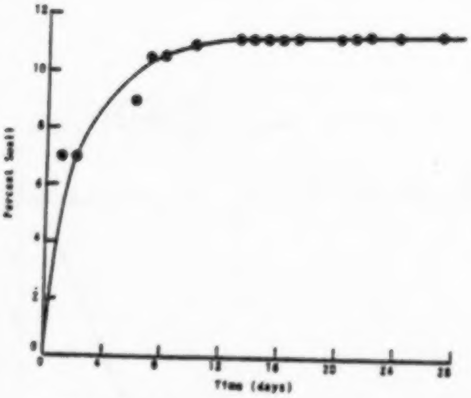

Figure 43. Swell Properties for Ranger Shale in methanol*
(See Table A20)

*Note: During the course of this test a dense bacterial or fungal growth occurred throughout the liquid and the clay. This growth undoubtedly affected the measured swell.

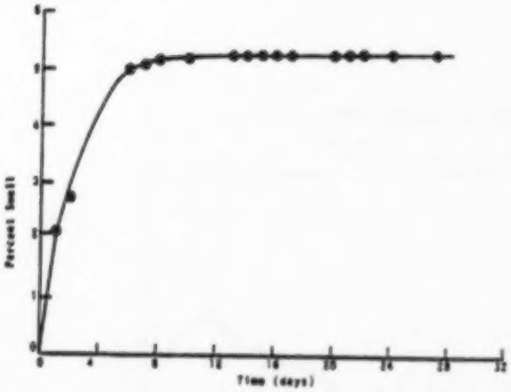

Figure 44. Swell properties for Ranger Shale in glycerol

(See Table A21)

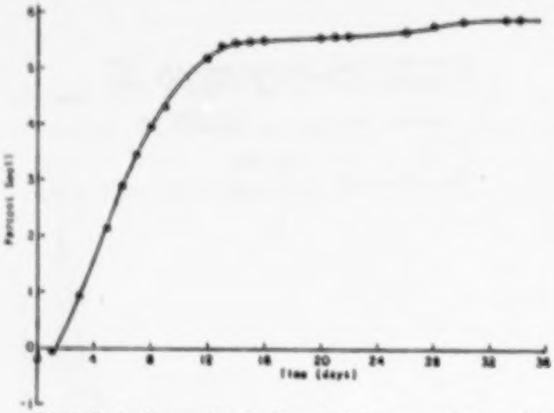

Figure 45. Swell properties for Ranger Shale in mixture of acetone (25 mole%) and benzene (75 mole%)
(See Table A22)

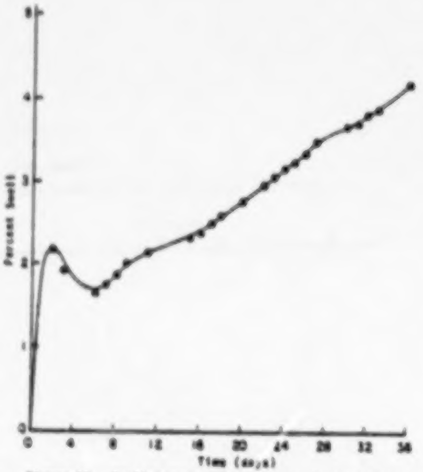

Figure 46. Swell properties for Ranger Shale in mixture of acetone (50 mole%) and benzene (50 mole%)
(See Table A23)

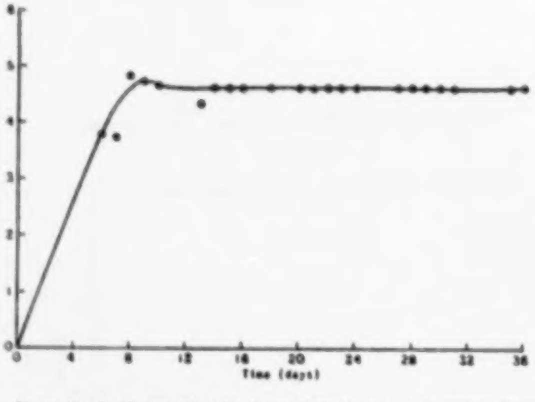

Figure 47. Swell properties for Ranger Shale in mixture of acetone (75 mole%) and benzene (25 mole%)
(See Table A24)

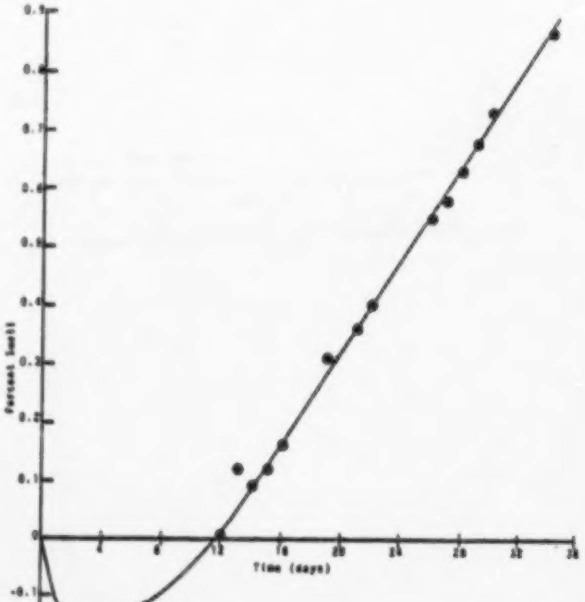

Figure 48. Swell properties for Ranger Shale in 50 volume percent mixture of xylene and deionized water
(See Table A25)

the pure benzene solution (Figure 25). The clay-soil swelled after the first day by about 5.5 percent during the following two weeks' exposure. That percent swell was maintained for the following three weeks when the test was terminated. The Ranger Shale swelled to a greater extent when exposed to the 25/75 acetone/benzene mixture than when exposed to either pure benzene (about 0.05 percent) or pure acetone (net 4 percent in two days) (Figure 36).

Tne 50/50 mole percent acetone/benzene mixture caused Ranger Shale to swell by about 2.2 percent during the first two days' exposure, shrink by about 0.4 percent by day 6, then to steadily swell by a net of 4 percent when the test was terminated (day 36) (Figure 46). Equilibrium was not apparently reached during that time. The 75/25 mole percent acetone/benzene mixture caused the Ranger Shale to behave in a manner similar to when it was exposed to pure acetone (Figures 47 and 36). Response to the mixture was not rapid as it had been in the pure solvent, however,

The 50/50 volume percent xylene/deionized water immiscible mixture (Figure 48) caused the Ranger Shale to shrink by about 0.15 percent during the first four days (as seen for pure xylene (Figure 27)), and then increase essentially linearly to a maximum of about 0.9 percent swell by day 34 when the test was terminated. Pure deionized water had caused the clay to equilibrate at a percent swell of about 11 percent after several days exposure.

The 50/50 volume percent acetone/water mixture caused Ranger Shale to equilibrate at about 11 percent swell after about one week of exposure (Figure 36). This response was essentially the same as the response to exposure to pure water (Figure 39).

Discussion

One of the clay-soils (Ranger Shale) contained measurable amounts of montmorillonite. Montmorillonite is an expandable layered silicate mineral, each layer consisting of an aluminum octahedral sheet between two tetrahedral silicate sheets. The forces holding the negatively charged montmorillonite layers together are weak electrostatic interactions between the exchangeable interlayer cations and either the surface oxygen (if one adopts the Hoffman-Endell-Wilson structure) or the surface hydroxy groups (if the Edleman-Favejce structure is accepted) (Theng, 1974).

X-ray investigations have shown that water or other polar liquids can penetrate into the interlamellar regions of montmorillonite and cause expansion along the c-axis. Olejnik et al.

(1974) have pointed out that the degree of swelling (as measured by X-ray diffraction) of montmorillonite in water depends on a variety of factors including the polarizing power of the exchangeable cation, the hydrostatic pressure, and the salt concentration of the swelling liquid solution. For the case of non-aqueous solvents, Barshad (1952) examined the effect of the dielectric constant of the immersion liquid on interlayer spacing and found that the degree of swelling of dehydrated montmorillonite and vermiculite increased with increasing dielectric constant when the clays were immersed in polar liquids (such as alcohols and ketones) of similar dipole moments. However, low dielectric liquids such as benzene, pentane, hexane and octane caused no interlayer swelling as detected by X-ray diffraction. Since mechanical swelling of clays in low dielectric media was observed in the current study using the consolidometer, an explanation is required.

While the purpose of this study was neither to provide a detailed mechanism for the swelling process, nor to sort out the significance of each of the numerous molecular and ionic properties affecting that process, an attempt has been made to correlate the swelling data with certain bulk or molecular characteristics of the clays and solvents under investigation.

Since swelling experiments were done not with the pure clay but rather with a sample of the clay-soil containing water (optimum moisture content), the interlayer cations of the montmorillonite were probably hydrated to an appreciable degree before the clay was immersed in the test liquid. Walker (1961) demonstrated that this water of hydration is of two types: the first, Water I, is directly coordinated and thus strongly bound to the interlayer cation; the second, Water II, is indirectly linked to the cation through the primary hydration shell. This second type of water is more labile than the first and hence more susceptible to replacement. Interlayer swelling of Ranger Shale in a given liquid can, therefore, be attributed to any or all of the following:

1. Direct solvation of an unsolvated or partially solvated interlayer cation (Type I interaction).
2. Indirect solvation of interlayer cations through bridging water molecules (Type II interaction).
3. Replacement of either Type I or Type II water, or both, by molecules of the immersion liquid. This would only be expected for highly polar molecules.

Evidence that water and polar organics generally interact with exchangeable cations to cause interlayer swelling, rather than with the negatively charged silicate sheets, has been provided by infra-red spectroscopy (Mortland, 1970). For a given clay sample, it seems reasonable that properties such as the dipole moment and the polarizability of the molecules of the immersion liquid, or the bulk dielectric constant of the liquid itself, should be related to the degree of swelling.

It is known that the interlayer swelling discussed above can cause at most a doubling of the volume of the dry clay. The greater degree of swelling often observed for montmorillonite and other clays requires that a second mechanism be postulated.

The surface of a clay particle can be thought of as a negatively charged area on which water molecules are adsorbed and to which cations are attracted by coulombic forces. Because of thermal agitation, cations are not rigidly bound to the surface but instead form a diffuse ion layer (diffuse double layer) whose average distance from the negatively charged surface depends upon such factors as ionic charge and dielectric constant of the medium in which the particle is immersed (typically water). The interaction of the diffuse ion layers associated with two adjacent particles is important in determining the extent of swelling.

Interparticle swelling can be envisioned to occur in the following manner. If a clay is immersed in water, there will be a tendency for the water to be adsorbed at negative particle surfaces, as long as the free energy of the adsorbed water is lower than that of the free water. This adsorbed water will force adjacent particles apart causing expansion. Van Olphen (1963) refers to this stage as short range particle interaction, or swelling due to surface hydration. It has been estimated (Yong and Warentin, 1975) that when the inter-particle distance exceeds about 15 Å, diffuse ion layers -- ones associated with each particle surface -- begin to form. Since the concentration of ions is higher in the region between particles than in the pore water itself, water molecules will move in response to this concentration gradient into the interlayer region. Additionally, so-called "osmotic swelling" results. Van Olphen (1963) calls this longer-range particle interaction either osmotic swelling or electrical double layer repulsion.

X-ray data obtained in the current study show that the various solvents used did not cause interlayer swelling to occur. It can be concluded, therefore, that the expansion of clays observed in consolidometer tests was the result of some combination of short-range and long-range repulsion between particles, that is, interparticle swelling.

For double layer repulsion, those factors which tend to increase the extent of the double layer near a particle surface also tend to increase the swelling potential of a clay or soil (Mitchell, 1976, p. 118). According to the Gouy theory, double layer thickness, 1/K, is determined by the following relationship:

$$(1/K) \doteq [(\varepsilon kT) / (8\pi n_o e^2 z^2)]^{\frac{1}{2}} \qquad (37)$$

where ε is the dielectric constant, n_o is the electrolyte concentration, z is cation valence, e is the unit electrical charge, k is the Boltzmann constant and T is absolute temperature. From this it can be seen that an increase in dielectric constant of the immersion fluid should cause an increase in the thickness of the diffuse double layer near a particle and that this should lead to enhanced repulsion and swelling.

Table 20 presents the dipole moments and dielectric constants for the solvents tested and the resulting swell for Ranger Shale, Kosse Kaoline and Fire Clay. First, it should be noted that even the two substances having zero dipole moment, carbontetrachloride and benzene, caused some expansion of clay exposed to it. Second, and more importantly, it can be seen that there is a rough relationship between the degree of expansion and the magnitude of the dielectric constant, as predicted by the Gouy Theory and as shown in Figures 48 a, b, and c. (Plots of percent swell vs ε (dielectric constant) showed better linearity than plots using $\varepsilon^{\frac{1}{2}}$ as might be suggested in equation 37.)

In Figures 49 through 51, percent swell caused by each solvent is plotted as a function of the solvent's dielectric constant for each of the three clays studied. In all cases, the solvents with high and intermediate dielectric constants (water and acetone, respectively) caused the clays to swell much more than those solvents in the low dielectric range (benzene, xylene, carbon tetrachloride and trichloroethylene). The deviation from linearity suggests that during swelling experiments some of the adsorbed water remained attached to the clay surface. This would cause the dielectric constant to be higher than expected.

Interestingly, the montmorillonite content of the clays appeared to have little effect on the degree of swelling. That is, Ranger Shale, which was the only clay-soil to contain montmorillonite, swelled 11.7 percent in water, the same as Kosse Kaoline which contained no measurable montmorillonite. The solvents with low dielectric constants caused about the same degree of swelling in all three clays. The fact that there is no correlation between the percent expandable layer silicate (montmorillonite) and the degree of swelling reaffirms the conclusion that for these systems, interlayer expansion is of relatively little importance.

Not shown in Figure 49 is the point for methanol. Ranger Shale swelled more than 11 percent in this solvent but the result was vitiated by the fact that a dense bacterial or fungal growth occurred throughout the liquid and the clay. It seems

TABLE 20. PERCENT SWELL OF TEST CLAYS IN CONTACT WITH LIQUIDS COMPARED TO DIELECTRIC CONSTANTS AND DIPOLE MOMENTS OF LIQUID

Immersion Liquid	Dielectric* Constant	Dipole* Moment (Debyes)	Equilibrium Percent Swell		
			Ranger Shale	Kosse Kaoline	Fire Clay
Water	79.38	1.82	11.7	11.7	8.2
Glycerol	42.5	-	5.3	-	-
Methanol	32.7	2.87	11.4**	-	-
Acetone	20.70	2.69	4.0	8.7	3.6
Trichloroethylene	3.42	0.80	1.0	0.6	0.1
Carbon tetrachloride	2.24	0.0	1.1	-0.03	-0.6
Benzene	2.28	0.0	0.05	-	1.3
Xylene	2.32	0.3	-0.11	0.16	-0.25

*After Riddick and Bunger (1970).

**See text discussion.

Dash (-) indicates not tested.

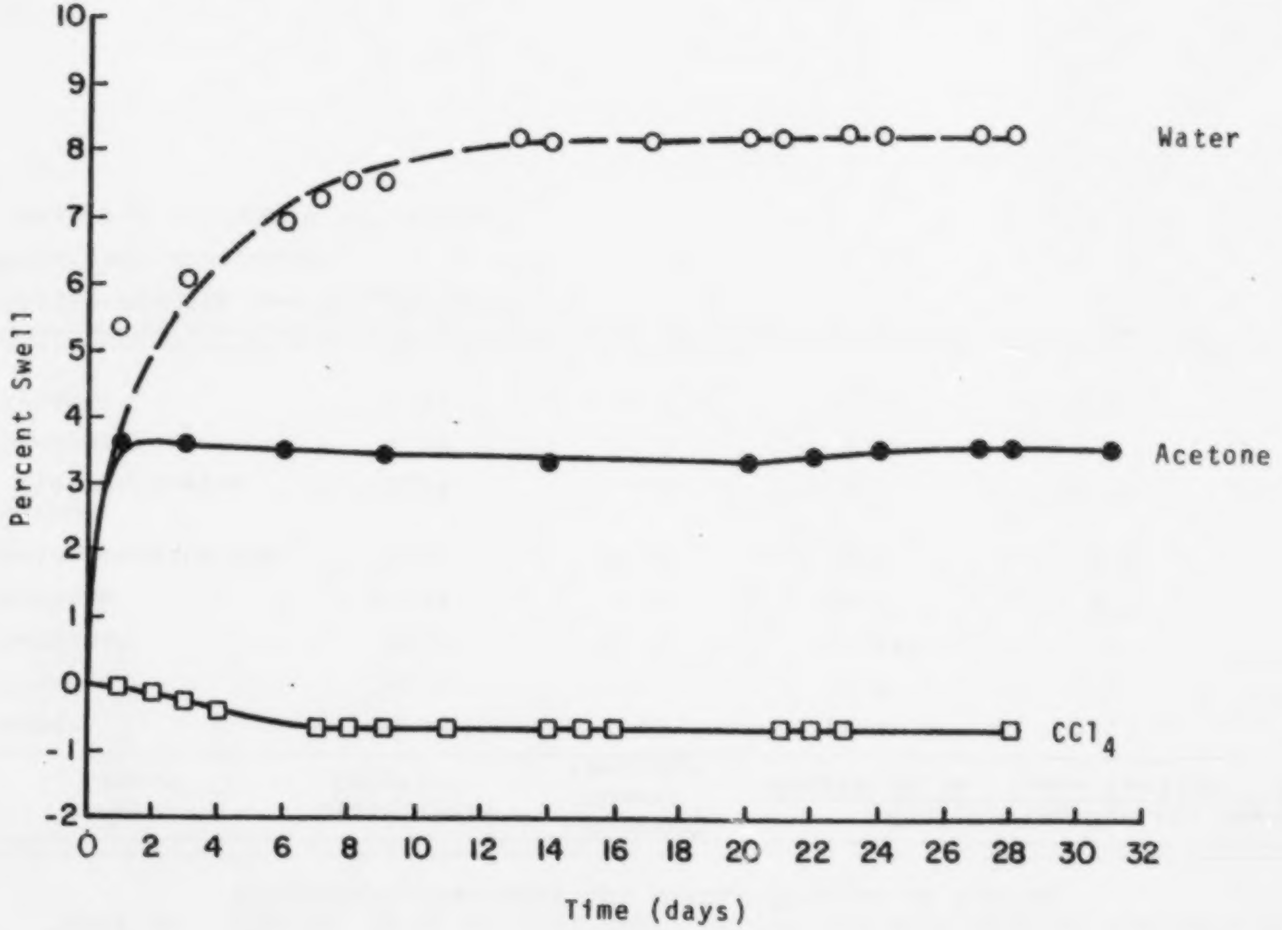

Figure 48a. Comparison of Swell Properties of Fire Clay in CCl_4, Acetone, and Water: Effects of Low, Intermediate, and High Dielectric Solvents

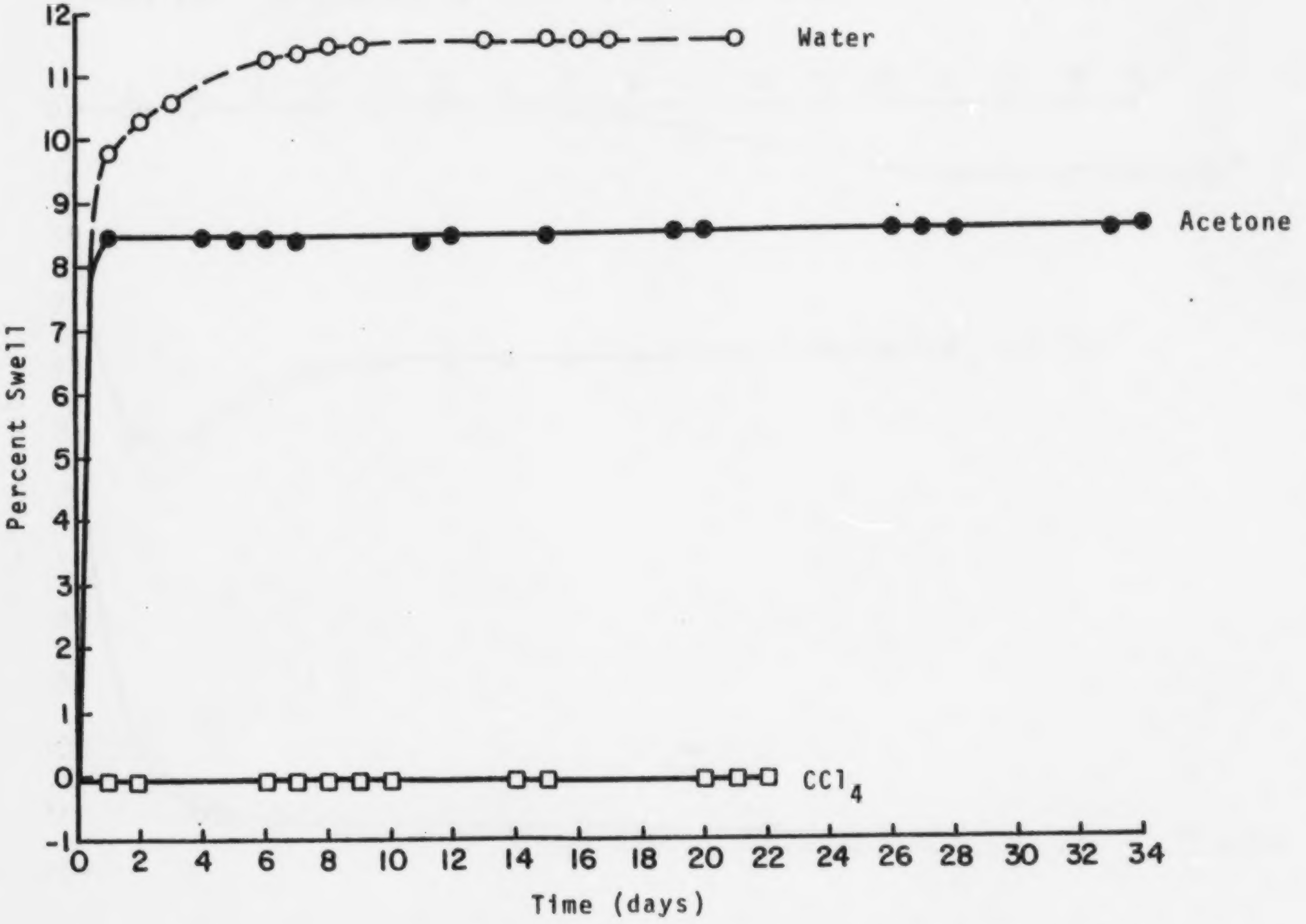

Figure 48b. Comparison of Swell Properties for Kosse Kaoline in CCl_4, Acetone, and Water: Effects of Low, Intermediate, and High Dielectric Solvents

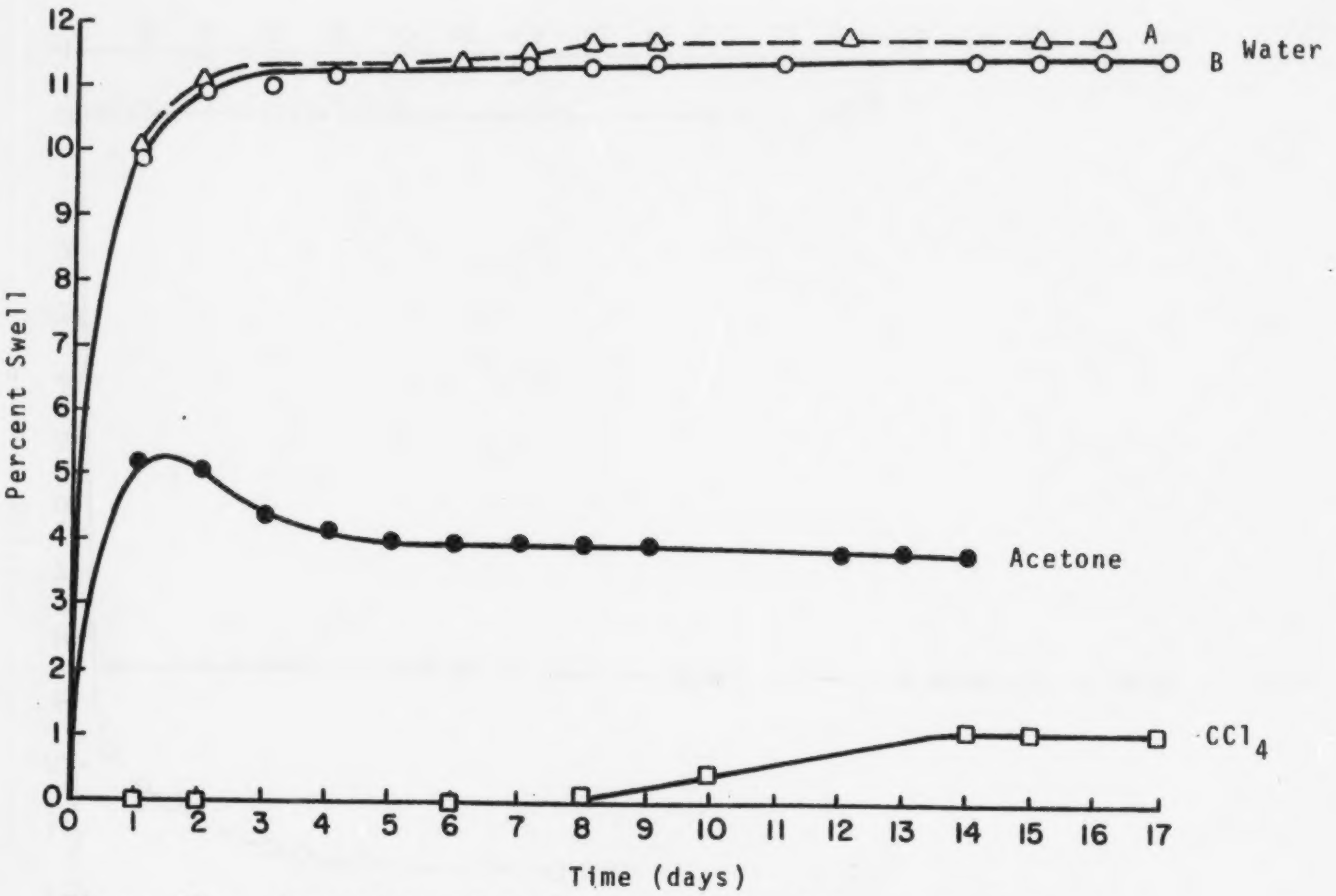

Figure 48c. Comparison of Swell Properties of Ranger Shale in CCl_4, Acetone, and Water: Effects of Low, Intermediate, and High Dielectric Solvents

A and B are duplicate runs.

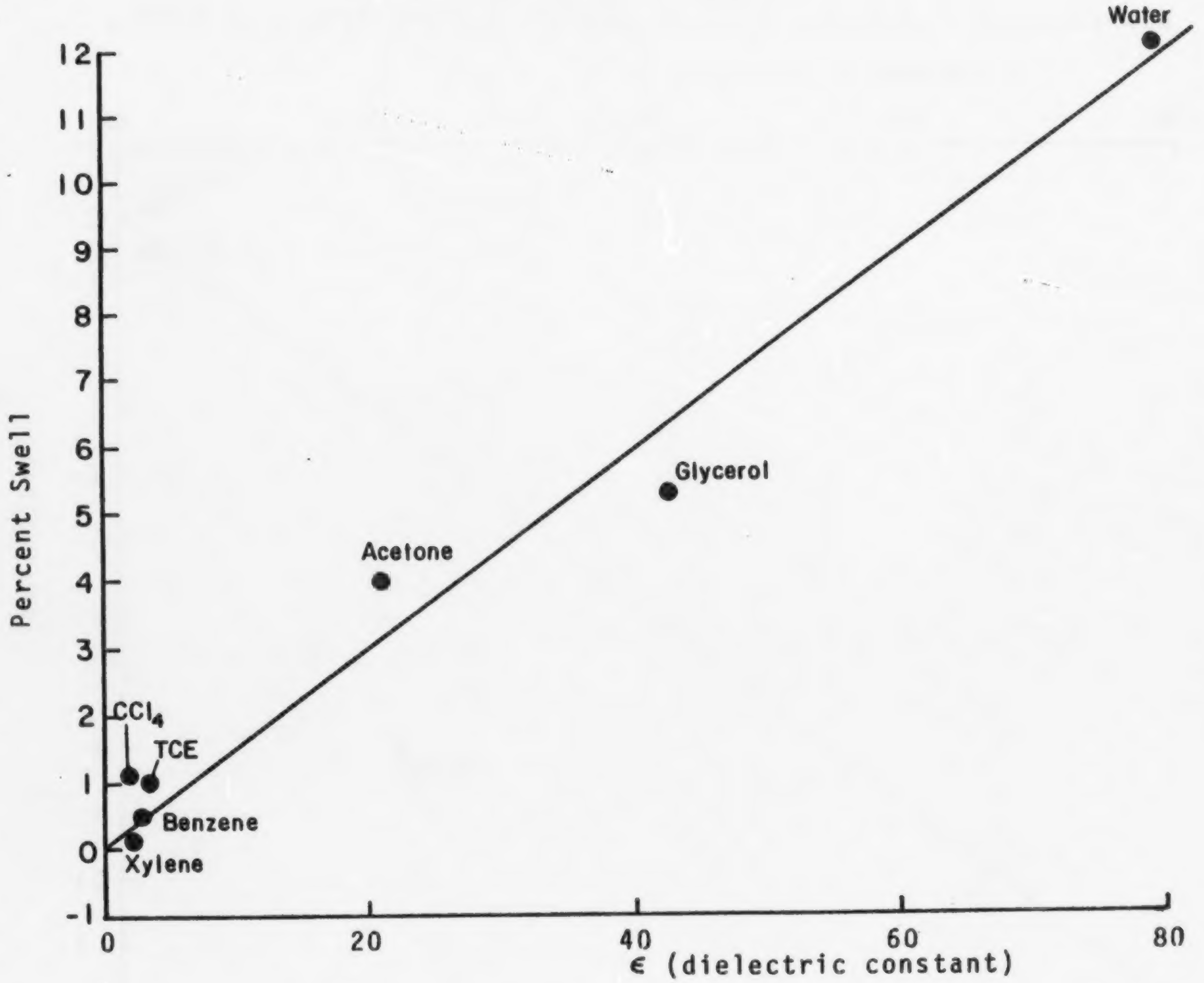

Figure 49. Relationship between solvent dielectric constant and percent swell of Ranger Shale

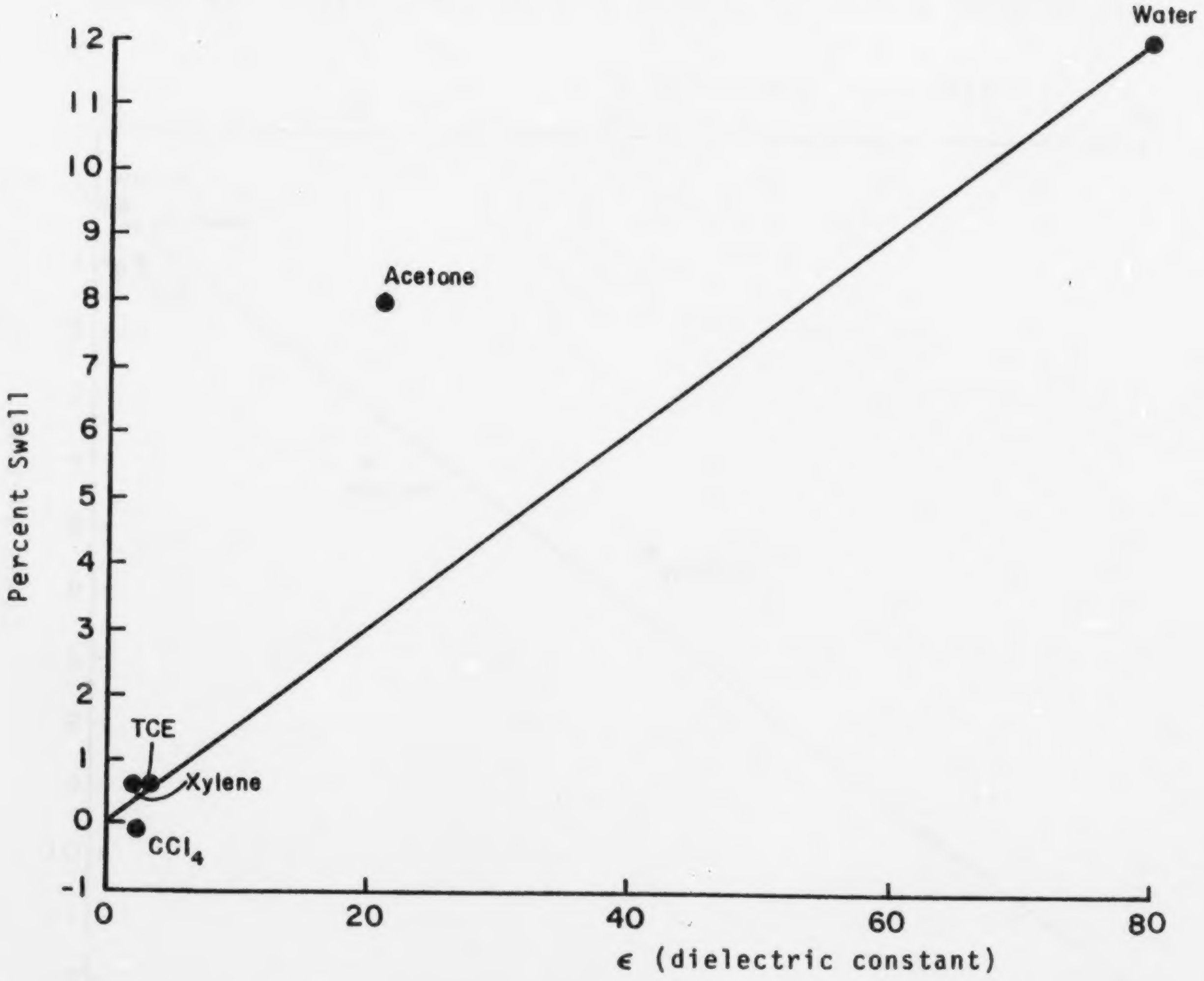

Figure 50. Relationship between solvent dielectric constant and percent swell of Kosse Kaoline

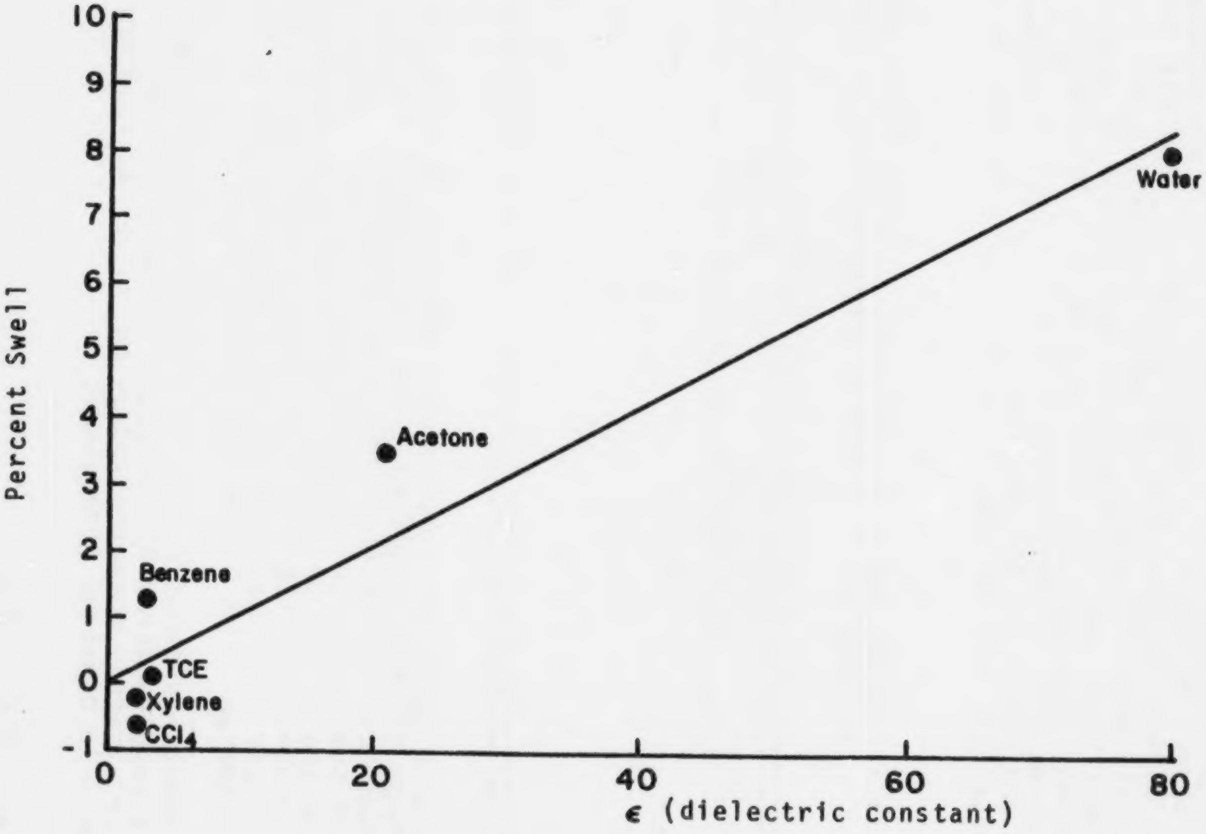

Figure 51. Relationship between solvent dielectric constant and percent swell of Fire Clay

clear that the extent of swell was influenced by this growth. The phenomenon should provide an interesting future investigation.

While the dielectric constant of the solvent plays the major role in determining swell properties, a more subtle factor for the hydrophobic solvents is the percent organic carbon content of the clay. In Table 21, degree of swelling and milligrams organic carbon per gram clay are presented. For all these three hydrophobic solvents studied on three clay-soils, an increase in percent swell was observed with an increase in organic carbon content from Fire Clay with 0.3 mg C/g, to Kosse Kaoline with 1.2 mg C/g, to Ranger Shale with 2.8 mg C/g. This is likely the result of Van der Waal's interactions between solvent molecules and the organic substances contained in the clay-soils.

TABLE 21. PERCENT SWELL OF CLAYS DUE TO HYDROPHOBIC SOLVENTS IN RELATION TO ORGANIC CARBON CONTENT OF CLAY

(values are percent swell)

Solvent	Fire Clay (0.3 mg C/g)	Kosse Kaoline (1.2 mg C/g)	Ranger Shale (2.8 mg C/g)
Xylene	-0.25	0.16	-0.11
CCl_4	-0.6	-0.03	1.1
TCE	0.1	0.6	1.0

For a number of clay-solvent mixtures, the phenomenon of shrinkage has been observed. The clay-organic systems have therefore been classified into four categories, depending on whether they exhibited only swelling, only shrinkage, or some combination of the two (Table 22). Typically, those solvents which caused swelling only were polar liquids while those which caused only shrinkage were apolar. However, there is no one generalization that can be applied to Table 22.

The behavior of a clay in a given organic solvent depends upon a complex array of factors. Thermodynamic equilibrium will be attained once the following two conditions are satisfied (where μ is chemical potential):

a. $$\mu^{H_2O}_{clay} = \mu^{H_2O}_{soln.} \qquad (38a)$$

b. $$\mu^{org}_{clay} = \mu^{org.}_{soln.} \qquad (38b)$$

Condition 38a states that the chemical potential of the water in the clay is equal to the chemical potential of water in the organic solvent. Condition 38b states that the chemical potential of the organic in the clay is equal to the chemical potential in the solution (traces of water dissolved in organic liquid).

TABLE 22. CLASSIFICATION OF CLAY-ORGANIC SOLVENT SYSTEMS ACCORDING TO SWELL PROPERTIES

Swelling Only	Swelling Then Shrinking	Shrinking Then Swelling	Shrinking Only
R.S./H_2O	R.S./Acetone	R.S./Benzene	R.S./Xylene(N.S.)
R.S./Gylcerol	K.K./Xylene	K.K./TCE	K.K./CCl_4(N.S.)
R.S./Methanol	F.C./Acetone	F.C./Benzene	F.C./CCl_4(N.S.)
R.S./CCl_4	F.C./TCE		
R.S./TCE	F.C./Xylene(N.S.)		
K.K./Water			
K.K./Acetone			
F.C./Water			

R.S. = Ranger Shale
F.C. = Fire Clay
N.S. = Net Shrinkage (Net Swell observed unless indicated otherwise)
K.K. = Kosse Kaoline
TCE = Trichloroethylene

Two transfer processes occurred during the experiment, namely, the transfer of some water from the clay to the solvent, that is dehydration of the clay; and transfer of solvent from the liquid into the clay. Depending on which one of these processes predominated at equilibrium, the clay would either swell or shrink. For those clay/solvent systems which undergo swelling, there is a net transfer of liquid into the clay; for those systems which undergo shrinkage, there is net transfer in the opposite direction.

The factors which favor movement of water out of the clay are a) interlayer cations with small charge/radius ratio, and b) relatively high water solubility in the organic liquid.

Factors which tend to favor movement of the organic into the clay are a) weak intermolecular forces in the liquid itself, and b) strong interactions of the organic molecules either with clay cations or with organic materials found in the clay.

The situation as outlined above is sufficiently complex at the molecular level to preclude predicting at this time the effect of a given solvent on a given clay. Even an analysis of the elemental composition of the clays has not provided the basis for a rationalization of the observed behavior in terms of interactions at the molecular level.

While the degree of swelling depends upon thermodynamic factors, the rate is a matter of kinetics. Whether swelling precedes shrinking or vice-versa is determined by the relative rates of transfer of water out of the clay and for organic solvent into the clay matrix. Table 22 shows that, in most cases, the latter process occurs more rapidly causing swelling of the clay.

The behavior of carbon tetrachloride and xylene deserves additional comment. Of all of the solvents studied these were the only ones which caused a net shrinkage to occur in some of the clays (see Table 22). Carbon tetrachloride caused Kosse Kaoline and Fire Clay to shrink while xylene brought about shrinkage of Ranger Shale and a net shrinkage (after initial swelling) of Fire Clay. In all experiments involving these solvents there was shrinkage at some time during the run. In column tests discussed in the next section, xylene, benzene, and carbon tetrachloride tended to "break through" the clay plug in the permeameter chamber, that is, they exhibited bulk flow, often instantaneous, through the column. This phenomenon can probably be attributed to the fact that these solvents cause clay shrinkage, which results in the formation of channels either in the bulk of the clay or between the clay and the permeameter walls. This points out the possibility that under field conditions, solvents which cause shrinking and cracking of liners might be transmitted abruptly, in bulk, to the surrounding groundwater. Based on this study, however, the problem should be expected only for solvents of low dielectric constant in the absence of water.

Since industrial wastes will, in most instances, be disposed of as mixtures, an effort was made to understand how simple binary solutions behave and to explain this behavior, where possible, in terms of the properties of the individual components. Swell properties were determined for Ranger Shale in three acetone/benzene mixtures ranging in composition from 25 to 75 mole percent; in an immiscible mixture of xylene and deionized water; and in an acetone/water solution. The results are summarized in Table 23.

TABLE 23. SWELL PROPERTIES OF RANGER SHALE IN FIVE SOLVENT MIXTURES

System	Percent Swell	Comment
25 mole% acetone/ 75 mole% benzene	5.75	
50 mole% acetone/ 50 mole% benzene	5.7	System not at equilibrium
75 mole% acetone/ 25 mole% benzene	4.6	
50 volume% xylene/ 50 volume% water	0.8	System far from equilibrium
50 volume% acetone/ 50 volume% water	11	
benzene	0.05	Net swell
acetone	4	
xylene	-0.11	Net shrink
water	11.7	

The conclusion drawn from these data is that in mixtures of solvents, a clay will tend to swell as though it were immersed in the component of higher dielectric constant only. That is, Ranger Shale swelled about 11 percent both in pure water and in the 50 percent acetone/water mixture. In the three acetone/benzene mixtures, the percent swell ranged from 4.6 to 5:75, which compares closely to the 4 percent swell observed for Ranger Shale in pure acetone. Thus it appears that a clay selectively sorbs that component of a miscible solvent mixture with which it can interact more (most) strongly. Since the driving force for swelling is the energy lost when surface or interlayer ions are solvated by molecules of the swelling liquid, it seems reasonable that the more polar component of the mixture (water in the case of acetone/water mixtures; or acetone in the case of acetone/benzene) should be preferentially imbibed by the clay.

The significance of this observation is that it suggests that in cases where a disposed solvent might cause a clay liner to shrink and crack (e.g., xylene or CCl_4), that solvent should be co-disposed of with a liquid such as acetone or water, which would prevent this from occurring. This possibility will be discussed in the next section.

Concluding Remarks

The swelling and shrinkage behavior of clays and soils in contact with water has been a subject of major interest to the civil engineer for many years. Swelling of soils can have a profound impact on the integrity of building foundations and pavement; cracking, often associated with shrinkage, can have adverse effects on the stability of dams and embankments.

In general, shrink-swell behavior has received little attention in the literature from those concerned with the storage of waste materials in landfills. For example, Sanks et al. (1975) investigated the suitability of clay beds for industrial waste storage and reported in some detail on the characteristics of the clays used. Fuller (1977), who studied the movement of various metals in soils also discussed a number of important factors to be considered in selecting disposal sites. In neither report, however, was shrink-swell behavior discussed.

Also virtually absent from the literature are reports dealing with the effects of organic liquids on the behavior of soil. As Mitchell (1976, p. 125) noted in his discussion of the effects of the low dielectric solvent ethanol on the extent of the diffuse double layer, "detailed consideration of the influence of dielectric constant may seem academic because the pore fluid in soils usually is water." Mitchell went on to say that there may be certain cases where oil or waste chemicals could be the pore fluid. These cases, however, have apparently not received wide attention.

The clays and soils used in this study all had low plasticity indices according to the criteria of Holtz and Gibbs (1956) and it is not surprising that the measured volume increases were generally small (maximum $\sim$ 12 percent), even for immersion in water. The greater degree of swelling observed for the Kosse Kaoline and Ranger Shale in water (11.7 percent) when compared with Fire Clay (8 percent) can be explained in terms of the higher plasticity indices for the former clays. The results here agree with expectations based on the work of Seed et al. (1964).

The observation that organic liquids caused swelling to occur in consolidometer tests but did not change the characteristic interlayer distance, d(001), for the clays, indicates that the mechanism for volume change is interparticle repulsion. This conclusion is supported by the fact that the high dielectric liquids cause greater swelling than low or intermediate dielectrics, in keeping with the general theory of clay particle interactions.

The clay organic content, recently discussed by Lee and Jones (1978) in relation to sorption, was established as an important factor governing the percent of swell of clays in nonionic hydrophobic solvents.

Shrinkage was observed for some clays in carbon tetrachloride and xylene, probably as a result of clay dehydration by these solvents. In nature, shrinkage of clay soils also occurs as the result of changes in moisture content and is often associated with cracking. The cracks formed in dehydrated clay soils can conduct wastes through an otherwise impermeable material (Yong and Warentkin, 1975). The results of this study suggest that certain solvents of low dielectric constant have an ability to cause shrinkage and cracking and might, therefore, cause damage to clay-lined pits. This implies that co-disposal measures, which have been discussed by Streng (1976) for hazardous inorganic wastes, might also be employed for spent industrial solvents. The results of work with mixtures in the current study suggest that low dielectric liquids be mixed with those of higher dielectric constant in such proportions as to give a smooth swelling curve.

EFFECTS OF ORGANIC SOLVENTS ON PERMEABILITY

The coefficient of permeability is probably the single most important laboratory-determined parameter for predicting the movement of hazardous solvents through clay liners. However, this is one parameter which can be measured only over long periods of time (typically on the order of a month), using equipment which is neither commercially available nor readily constructable. One of the objectives of this research has been to relate the coefficient of permeability to more readily measurable parameters of clays and solvents in order that permeability might be estimated under a variety of circumstances.

Results

Permeability data were collected on 15 clay/solvent systems. These data are presented in Appendix Tables B 1 through B 19. Figures 52 through 70 show the coefficients of permeability over time.

For most of the pure organic solvents tested, Ranger Shale showed patterns of decreasing permeability for the first five to ten days, before a plateau was reached. After eight days' exposure to benzene, Ranger Shale exhibited breakthrough (Figure 52). The permeability of Ranger Shale to xylene equilibrated after about ten days at 4×10^{-9} cm/sec (Figure 53); the permeability to carbon tetrachloride reached an apparent equilibrium of 25×10^{-9} cm/sec after about four days (Figure 54). Equilibrium permeability of Ranger Shale to trichloroethylene, 2×10^{-9} cm/sec, was reached after about two weeks whereas that of acetone, 2.5×10^{-9} cm/sec, was reached after approximately one month's exposure (Figures 55 and 56). Equilibrium permeability of Ranger Shale to methanol was about 15×10^{-9} cm/sec and was reached after about three weeks of exposure (Figure 57); for glycerol, permeability at equilibrium was 0.9×10^{-9} cm/sec after about a week's exposure (Figure 58). The permeability of Ranger Shale to deionized water remained more or less constant at about 38×10^{-9} cm/sec during the one month's monitoring period (Figure 59).

The permeability of Kosse Kaoline to m-xylene (Figure 60), acetone (Figure 61) and deionized water (Figure 62) appeared to decrease during the first week or so of exposure and then increase to a plateau level. For xylene an equilibrium permeability coefficient of about 50×10^{-9} cm/sec was reached after about 24 days; for acetone, the equilibrium was about 65×10^{-9} cm/sec and was reached after about three weeks; and for deionized water, equilibrium of 220×10^{-9} cm/sec was reached after about two weeks.

As was found for permeability of Kosse Kaoline to xylene, acetone, and water, the permeability of Fire Clay to xylene

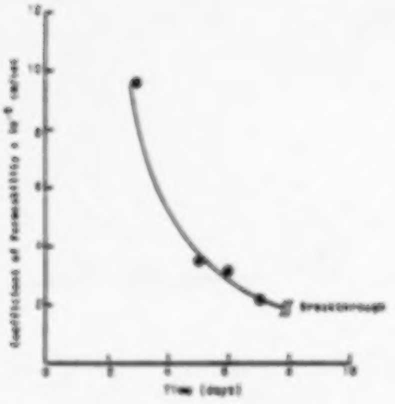

Figure 52. Coefficient of permeability of Ranger Shale to benzene

(See Table 61)

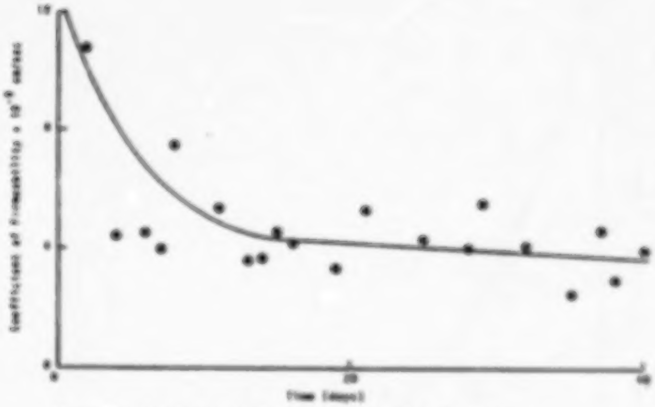

Figure 53. Coefficient of permeability of Ranger Shale to xylene

(See Table 62)

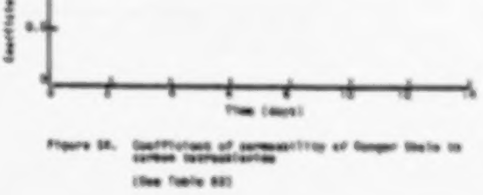

Figure 54. Coefficient of permeability of Ranger Shale to carbon tetrachloride

(See Table 63)

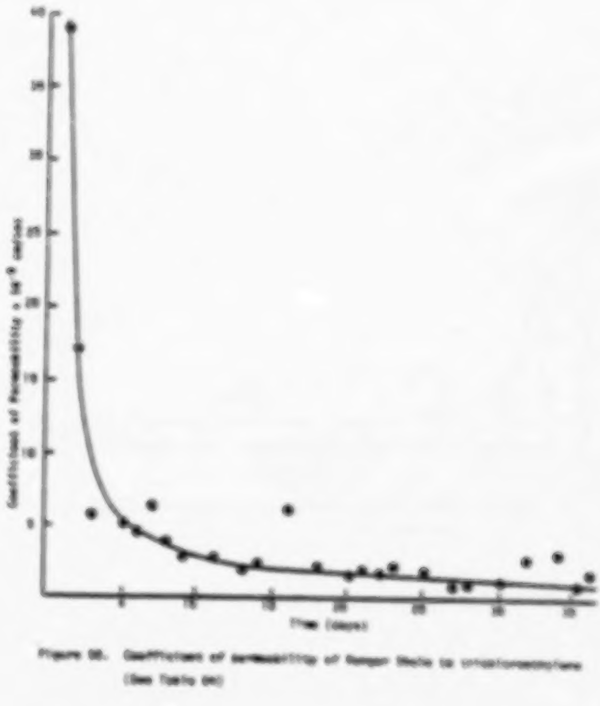

Figure 55. Coefficient of permeability of Ranger Shale to trichloroethylene

(See Table 64)

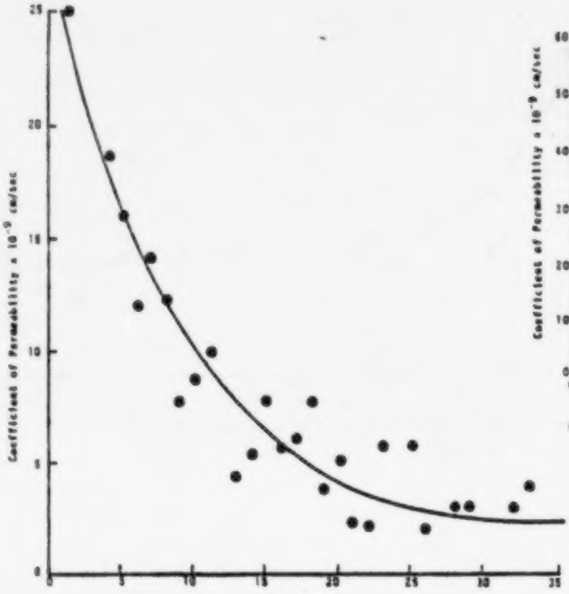

Figure 56. Coefficient of permeability of Ranger Shale to acetone
(See Table 85)

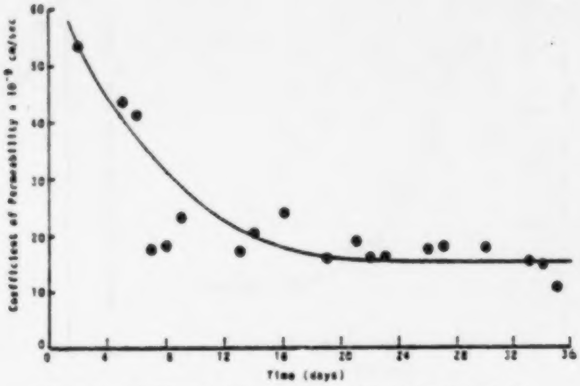

Figure 57. Coefficient of permeability of Ranger Shale to methanol
(See Table 86)

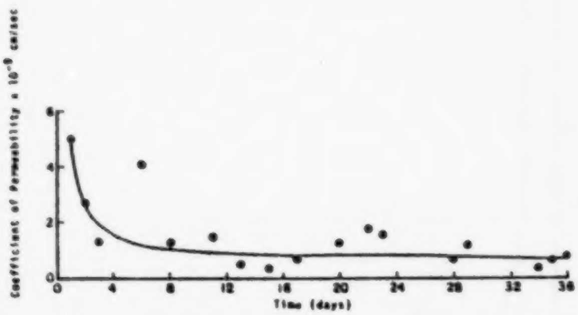

Figure 58. Coefficient of permeability of Ranger Shale to glycerol
(See Table 87)

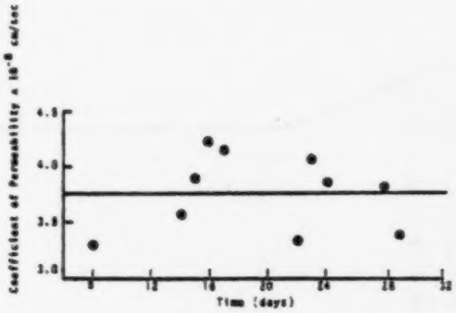

Figure 59. Coefficient of permeability of Ranger Shale to deionized water
(See Table 88)

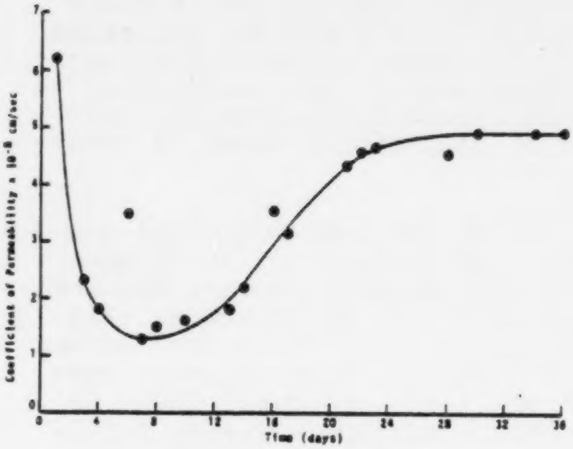

Figure 60. Coefficient of permeability of Kosse Kaoline to xylene (See Table B9)

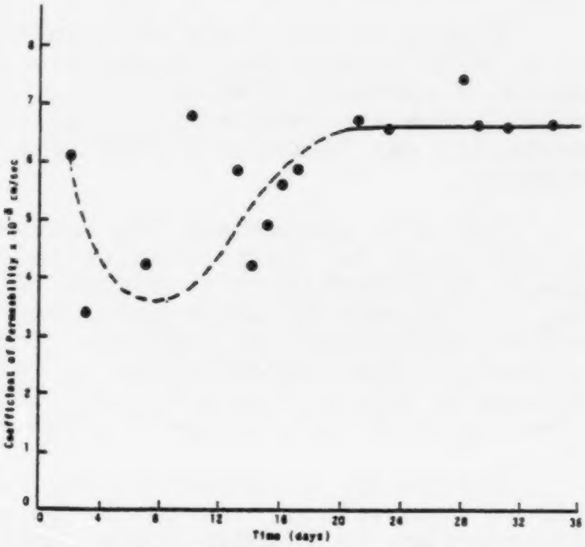

Figure 61. Coefficient of permeability of Kosse Kaoline to acetone (See Table B10)

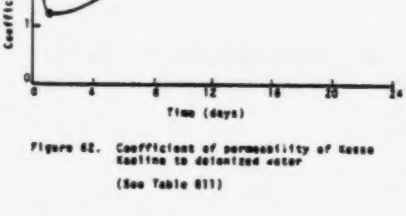

Figure 62. Coefficient of permeability of Kosse Kaoline to deionized water (See Table B11)

(Figure 63), acetone (Figure 64), and water (Figure 65) decreased in the first week of exposure, remained low for 1.5 to 2 weeks, and then increased. It appears that xylene broke through after maintaining a permeability coefficient of about 1×10^{-9} cm/sec. Equilibrium levels for acetone and deionized water were 7×10^{-9} and 13.5×10^{-9} cm/sec, respectively; both reached equilibrium after about four weeks. The coefficient of permeability of Fire Clay to trichloroethylene decreased over the first month of monitoring to an equilibrium level of about 2.5×10^{-9} cm/sec (Figure 66).

There was considerable scatter in the coefficient of permeability values for Ranger Shale with mixtures of 75/25 mole percent acetone/benzene and 50/50 mole percent acetone/benzene such that patterns over time were difficult to determine (Figures 67 and 68). Equilibrium values of about 7.5×10^{-9} cm/sec and on the order of 15 to 20×10^{-9} cm/sec, respectively, were found for those systems. The permeability of Ranger Shale to the 25/75 mole percent acetone/benzene mixture appeared fairly constant at about 5×10^{-9} cm/sec over time (Figure 69). Permeability behavior over time did not appear to be related to that found for either the benzene or acetone pure systems.

Figure 70 shows the permeability over time of Ranger Shale to a 75/25 mole percent acetone/carbon tetrachloride mixture. Behavior appeared similar to that for acetone alone, although equilibrium was reached more rapidly and the equilibrium permeability was somewhat higher (9×10^{-9} cm/sec) than that for acetone.

Table 24 summarizes the values of equilibrium permeabilities of the clays to the pure solvents tested. Ranger Shale showed greatest permeability to carbon tetrachloride and water (discounting the benzene breakthrough), and least permeability to glycerol, trichloroethylene and acetone. Both Kosse Kaoline and Fire Clay showed greatest permeability to water (discounting xylene breakthrough), followed by acetone. For all solvents tested, Kosse Kaoline was much more permeable than either Ranger Shale or Fire Clay.

Initially, experiments were carried out in an air conditioned room without careful temperature control. Large daily fluctuations in K under these conditions were probably due to changes in room temperature, which had the effect of increasing or decreasing the volume of fluid in the permeability chamber. This volume change was then reflected as a rise or drop of the meniscus in the 8 mm diameter graduated standpipe. After the initial runs with water and Ranger Shale, experiments were conducted in a temperature controlled room in order to minimize scatter in the data.

The most common pattern observed in the permeability data was an exponential decrease in K during the early stages of the

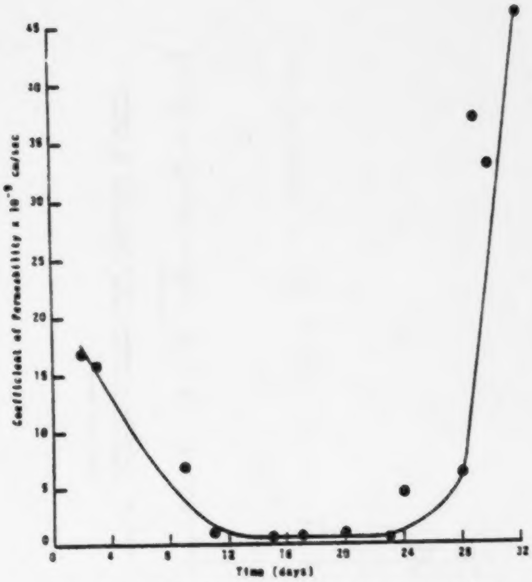

Figure 63. Coefficient of permeability of Fire Clay to xylene (See Table B12)

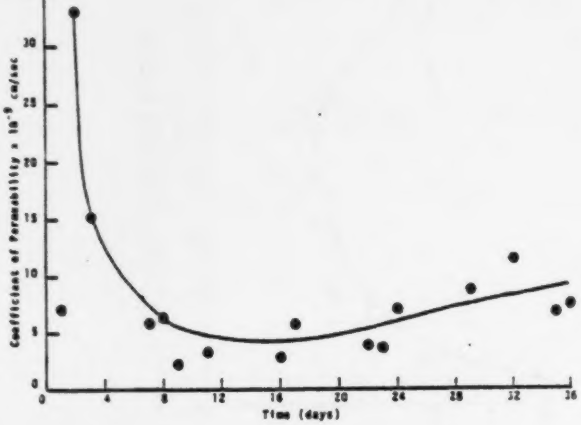

Figure 64. Coefficient of permeability of Fire Clay to acetone (See Table B13)

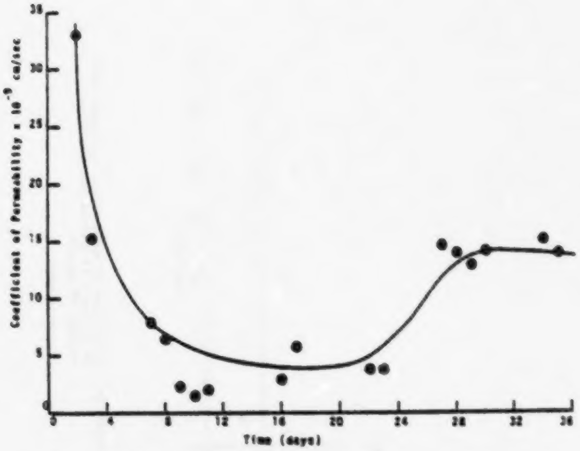

Figure 65. Coefficient of permeability of Fire Clay to deionized water (See Table B14)

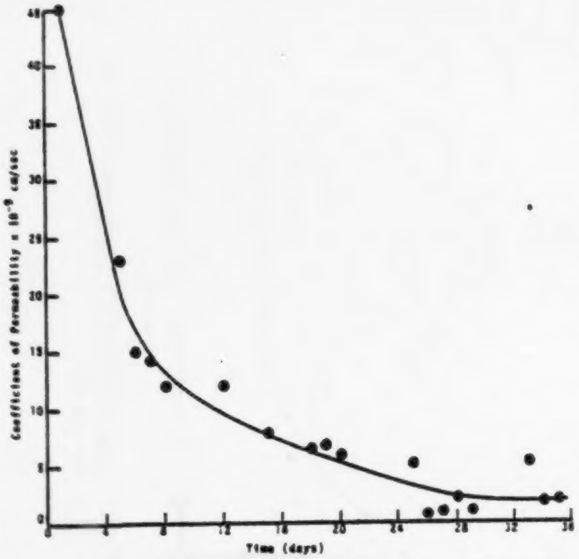

Figure 66. Coefficient of permeability of Fire Clay to trichloroethylene (See Table B15)

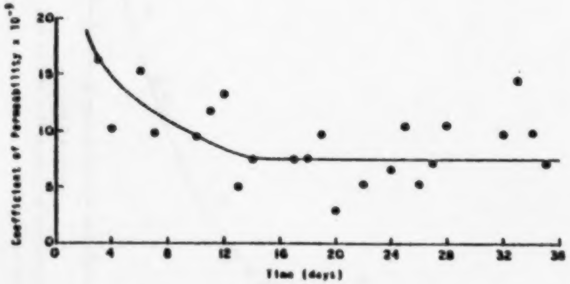

Figure 67. Coefficient of permeability of Ranger Shale to a mixture of acetone (75 mole%) and benzene (25 mole%)

(See Table B16)

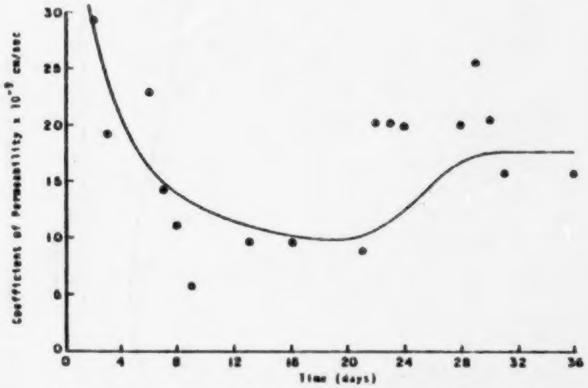

Figure 68. Coefficient of permeability of Ranger Shale to a mixture of acetone (50 mole%) and benzene (50 mole%)

(See Table B17)

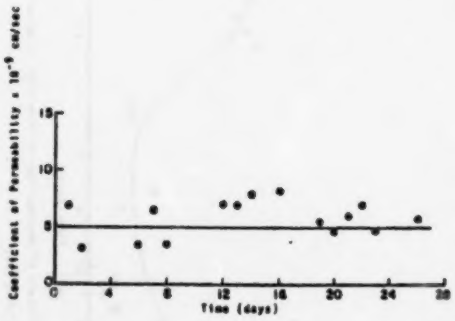

Figure 69. Coefficient of permeability for Ranger Shale to a mixture of acetone (25 mole%) and benzene (75 mole%)

(See Table B18)

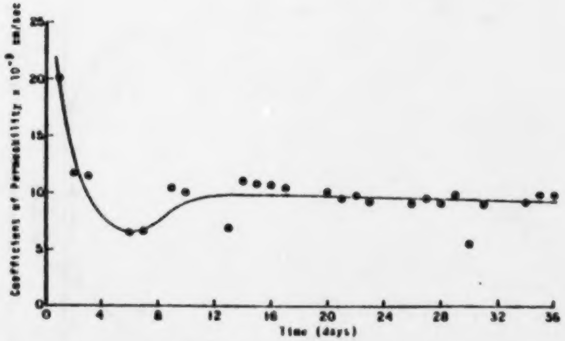

Figure 70. Coefficient of permeability of Ranger Shale to a mixture of acetone (75 mole%) and carbon tetrachloride (25 mole%)

(See Table B19)

TABLE 24. EQUILIBRIUM PERMEABILITIES OF CLAYS TO ORGANIC SOLVENTS AND WATER

(x 10^{-9} cm/sec)

	Ranger Shale	Kosse Kaoline	Fire Clay
Benzene	2 (Break)	-	-
Xylene	4	50	1 (Break)
Carbon tetrachloride	25	-	-
Trichloroethylene	2	-	2.5
Acetone	2.5	65	7
Methanol	15	-	-
Glycerol	0.9	-	-
Water	38	220	13.5

Dash (-) indicates not measured.

experiment followed by a gradual leveling off as the system approached equilibrium. Variations in K with time have been reported in the literature by a number of investigators (Allison, 1947; Bodman, 1937). Poulovassilis (1972) studied the factors governing this phenomenon for water and aqueous solutions in contact with natural clays and showed that by far the most pronounced reductions in K were caused by microbial production of gases, and consequent clogging of soil pores. Because of evidence for microbial activity observed during the sorption and swelling tests conducted during the current study, it is possible that the decline in K with time was due in part to microbial production of either CO_2 or CH_4 during the early stages of the experiment when organic concentrations in the column were still sufficiently low to be non-toxic (see Alexander, 1961 for a discussion of the effect of soil microorganisms on organic compounds).

In addition to microbially induced changes in K, changes arising from a reduction in the pore space geometry of the clay also seem plausible. Poulovassilis (1972) has used this explanation to account for the 15 percent decrease in hydraulic conductivity (coefficient of permeability) observed with sterilized soils where microbial action was not a factor.

What is perhaps most striking about the permeability data collected during the current study is the fact that each of the organic solvents when in contact with a given clay had equilibrium permeability values which were smaller than that of water on the same clay, by an order of magnitude in most cases. According to Davis and De Wiest (1966), the coefficient of permeability K, can be determined by:

$$K = cd^2\ (\gamma/\mu) \qquad (39)$$

where c = dimensionless constant or shape factor which includes grain size, packing and porosity,
d = average pore size of the porous medium,
γ = density of the solvent, and
μ = viscosity.

If the first two terms (c and d) are taken to be characteristic of the clay or soil, the coefficient of permeability will depend upon the ratio γ/μ. Table 25 presents γ/μ values for solvents evaluated in this study. Based on the equation above, most of the organic solvents would have been expected to move through Ranger Shale between 1.4 and 2.5 times more rapidly than water. The results of the current study, however, which showed that water had the highest permeability of all solvents tested, contradicted this prediction. It is interesting to note that it is likely that Equation 39 (basically γ/μ) which was developed based on permeabilityof saline solutions would likely have been used as a basis for estimating the permeability of organic wastes if this study had not been conducted. It is evident from the results of this study that this approach is not appropriate for organic solvents.

TABLE 25. DENSITY-VISCOSITY RATIOS FOR ORGANIC SOLVENTS AND WATER

Solvent	γ (g/cc)	μ	Ratio γ/μ
Water	1.0	1.0	1.0
Glycerol	1.26	1412	8.9×10^{-4}
Methanol	0.796	0.551	1.44
Acetone	0.79	0.32	2.46
Trichloroethylene	0.79	0.34	2.32
Carbon Tetrachloride	1.59	0.100	1.59
Benzene	0.879	0.649	1.35
m-xylene	0.60	0.50	1.20

After Riddick and Bunger (1970).

It was mentioned earlier that the swelling of grains tends to have a retarding effect on the transmission of fluids through a clay by decreasing the pore sizes. Data have been examined, therefore, for a possible correlation between the degree of swelling and the permeability. Table 26 lists the values for swell properties and coefficients of permeability for all single

TABLE 26. PERMEABILITIES AND PERCENT SWELL FOR ALL SINGLE SOLVENT SYSTEMS TESTED

Clay	Solvent	Percent Swell	Coefficient of Permeability ($\times 10^{-9}$ cm/sec)
Ranger Shale	Benzene	0.05	2 (Break)
	Xylene	-0.11	4
	Carbon tetrachloride	1.1	25
	Trichloroethylene	1	2
	Acetone	4	2.5
	Methanol	11.4	15
	Glycerol	5.3	0.9
	Water	11.7	38
Kosse Kaoline	Xylene	0.16	50
	Acetone	8.7	65
	Water	11.7	220
Fire Clay	Xylene	-0.25	1 (Break)
	Carbon tetrachloride	-0.6	2.5
	Acetone	3.6	7
	Water	8.2	13.5

solvent systems tested. It can be seen that the markedly smaller permeabilities of the organic solvents cannot be attributed to attenuation of flow through swelling. In fact, the solvent which caused each of the clays to undergo the greatest swelling, namely water, had the largest coefficient of permeability - a result which directly conflicts with expectations based on earlier work with aqueous solutions.

To account for the permeability results, it is necessary to consider how an organic molecule (or water) might move through a sorbing, porous medium containing interstitial water. Such a medium has been described by van Genuchten and Wierenga (1976) as consisting of the following five regions: (see Figure 71)

1. Air space
2. Inter-aggregate water
3. Intra-aggregate water

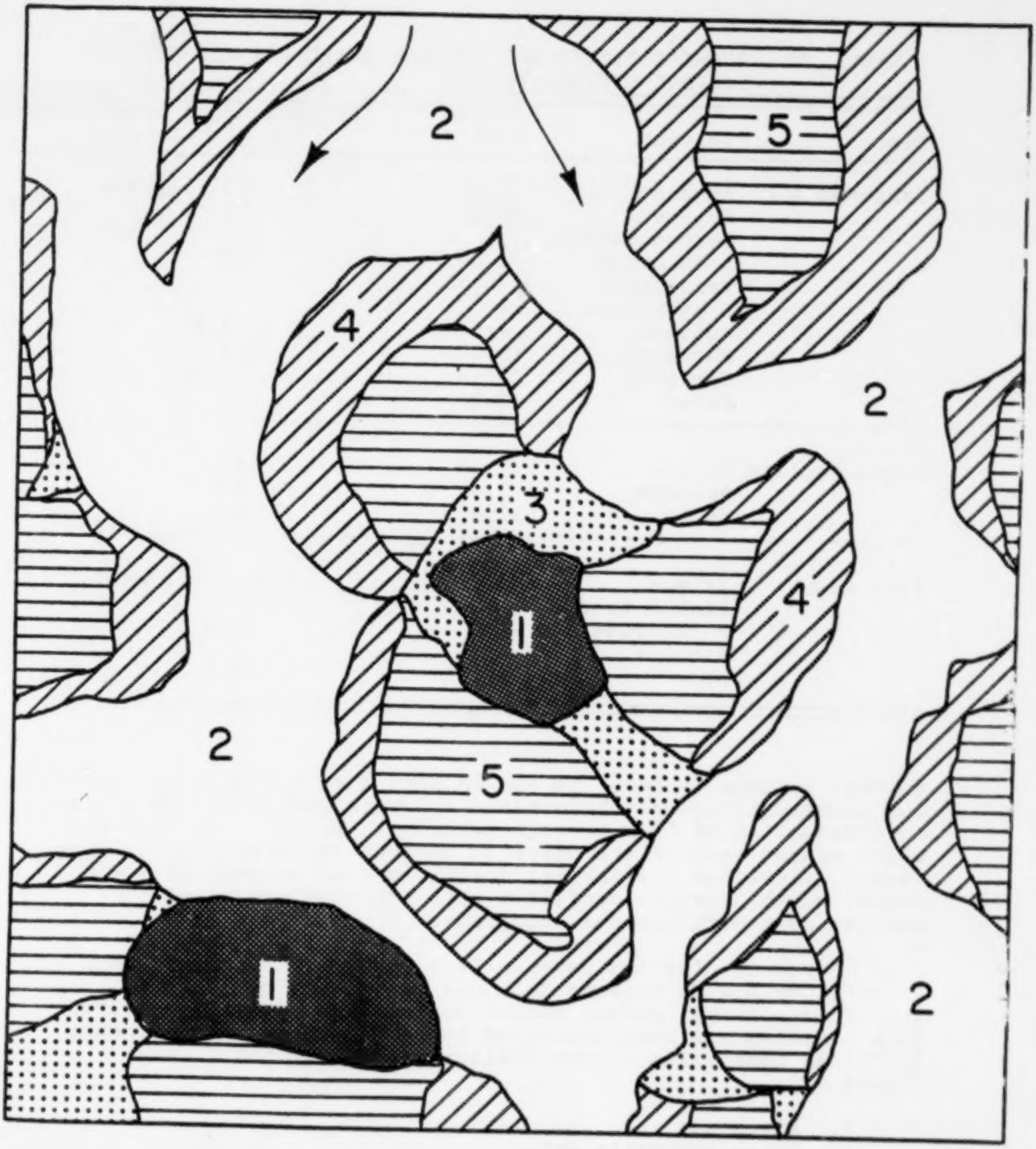

Figure 71. Representation of water-containing clay

After van Genuchten & Wierenga (1976)
(See text for discussion of areas)

4. A dynamic soil region, in contact with the inter-aggregate water, where sorption can occur readily
5. A stagnant soil region where sorption can occur only after organic molecules have diffused through the surrounding intra-aggregate water.

Molecules of the permeant move by diffusion and convection through the inter-aggregate water and at each stage along the way are partitioned between the aqueous phase and the dynamic soil region according to the Freundlich equation. Those molecules which are weakly sorbed by soil particles tend to move quickly through the aqueous channels. Hydrophobic substances such as benzene, xylene, carbon tetrachloride and trichloroethylene, which are highly partitioned at any instant onto the soil or clay phase, would be expected to have lower permeabilities than water and acetone. This model suggests a plausible correlation between the coefficient of permeability, which measures the rate of movement of the permeant along the column, and the octanol/water partition coefficient, which measures the tendency of permeant molecules to escape from the aqueous phase. Along these lines, Briggs (1973) has shown that the rate of movement of unionized pesticides through soils correlates with their octanol/water partition coefficients.

It can be seen in Table 27 that, in general, for a single clay-soil, the permeability of a liquid decreases as the log of its octanol/water partition coefficient, P, increases. Since P is a measure of escaping tendency of the material from water (Baughman and Lassiter, 1978), it seems reasonable that those substances least compatible with water should move most slowly through the column. This generalization seems to hold for solvents on Kosse Kaoline and Fire Clay, as can be seen when the coefficient of permeability is plotted against the log of the octanol/water partition coefficient for solvents on these clays (see Figure 72 and Table 27). In both cases, the more positive the value of log P, the smaller the value of K, or in other words, the more hydrophilic the organic, the more rapidly it moves through the clay. This relationship did not apply as consistently in the case of Ranger Shale, however. The three solvents which exhibited anomalous behavior may have done so for the following reasons:

1. Carbon tetrachloride. Despite a high value for log P, carbon tetrachloride had a coefficient of permeability much larger than that of the other hydrophobic solvents studied (i.e., benzene, xylene and trichloroethylene). This is possibly the result of its ability to cause clay shrinkage. This is discussed below.

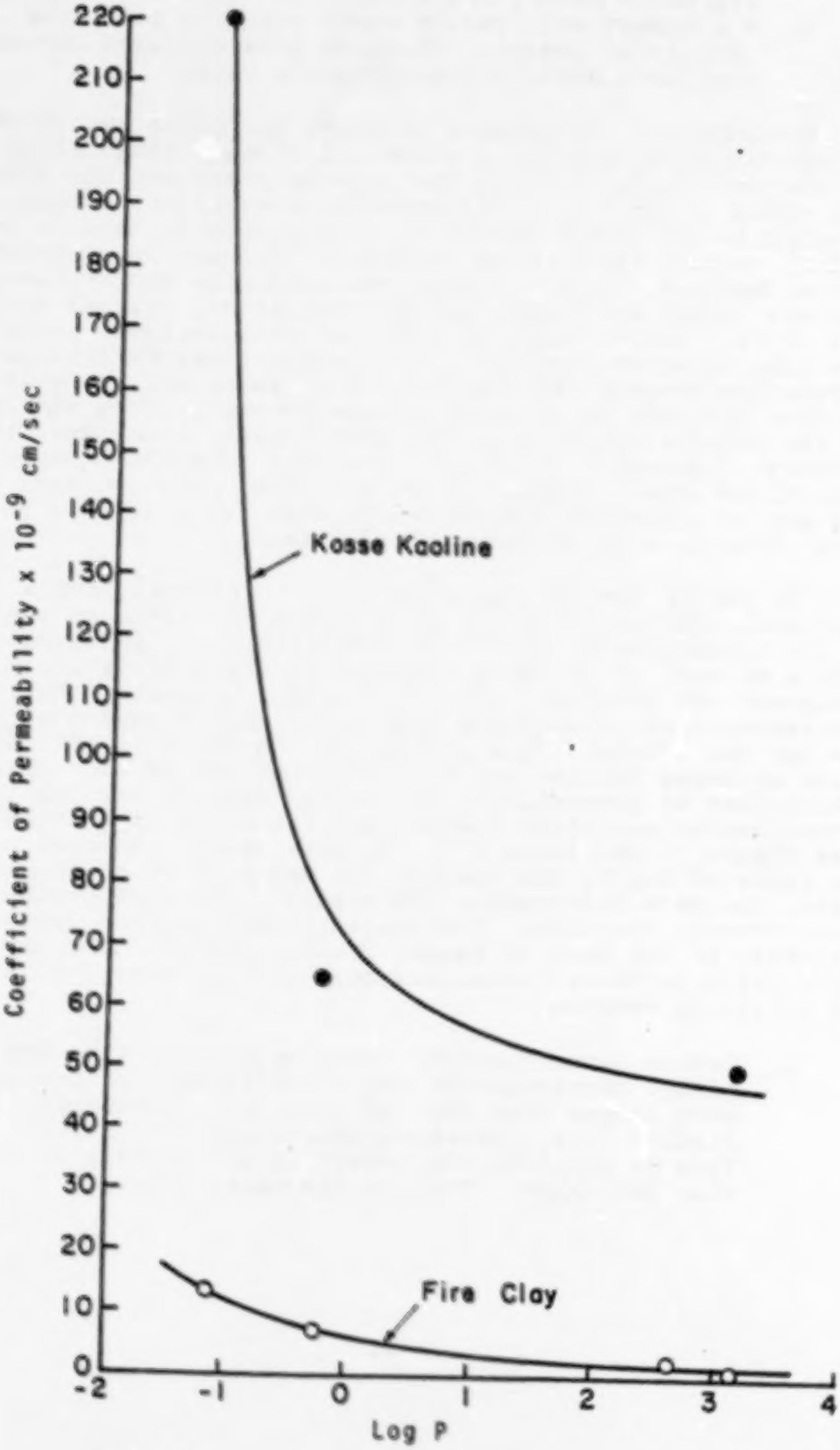

Figure 72. Relationship between coefficient of permeability and octanol/water partition coefficient

TABLE 27. PERMEABILITIES AND OCTANOL/WATER PARTITION COEFFICIENTS FOR SOLVENTS ON THREE CLAYS

Clay	Solvent	Equilibrium Coefficient of Permeability ($\times 10^{-9}$ cm/sec)	Log Octanol/Water Partition Coefficient
Ranger Shale	Benzene	2	2.13
	Xylene	4	3.15
	Carbon tetrachloride	25	2.64
	Trichloroethylene	2	2.37
	Acetone	2.5	-0.24
	Methanol	15	-0.32
	Glycerol	0.9	-2.56
	Water	38	-1.15
Kosse Kaoline	Xylene	50	3.15
	Acetone	65	-0.24
	Water	220	-1.15
Fire Clay	Xylene	1	3.15
	Carbon tetrachloride	2.5	2.64
	Acetone	7.0	-0.24
	Water	13.5	-1.15

2. Acetone. This is a hydrophilic substance having a negative value for log P; it would have been expected to move through the clay much more rapidly than benzene and xylene. That it did not suggests the possibility that microbial decomposition of acetone on the biologically active clay, Ranger Shale, resulted in CO_2 production and clogging of pores, thus reducing the observed permeability value.

3. Glycerol. This has a more negative log P value than water itself and would have been expected to permeate at a higher rate than water. Here, however, the extreme viscosity of glycerol (1400 cp as opposed to 1.0 cp for water) was clearly a factor in reducing flow. It should be noted, however, that glycerol permeates much more rapidly than would have been expected based on a simple comparison of its viscosity with that of water. Given this consideration alone, it should have moved at

1/1000th the rate of water. That in fact it had a K value of 1/36th that of water can be explained in terms of its high affinity for the aqueous phase. Work with glycerol suggests that viscosity is a factor that should be considered in any model of solvent flow through clays but it is clearly not as important as the hydrophilic or hydrophobic character (as measured by P or by ϵ) of the permeating substances.

There also appears to be a good relationship between the permeability of clay to a solvent and the solvent's dielectric constant, such that the greater the dielectric constant, the greater the value of K (Figures 73 through 75). This is not surprising in view of the above model, since the dielectric constant is another approximate measure of a liquid's hydrophobic or hydrophilic character. Substances with high dielectric constants tend to be hydrophilic and can therefore be expected to move more quickly through the aqueous channels in the clay. Low dielectric substances will be sorbed and thus retarded in their movement. The relationship between this parameter and the coefficient of permeability will be discussed at the end of this section.

A number of the systems clearly showed anomalous behavior with respect to the permeability - dielectric constant relationship; one of these was carbon tetrachloride/Ranger Shale. Here, the value of K was too high when compared with other solvents having similar dielectric constants and octanol/water partition coefficients. As noted earlier, of all the solvents studied, CCl_4 had the greatest tendency to cause shrinkage of clays. As a result of this shrinkage, channels were formed which allowed the solvent to flow through the system more readily. Measured permeability values were therefore higher than expected and this caused the point for CCl_4 to be far from the line of best fit in Figure 73. Glycerol, as discussed previously, had an unusually low permeability probably because of its high viscosity. This is reflected in its position in Figure 73.

Although the benzene/Ranger Shale system showed solvent breakthrough due to clay shrinkage during several permeability tests, it appeared to fit the general relationship between permeability and dielectric constant shown in Figure 73. Fire Clay in xylene also showed solvent breakthrough eventually. The point for this system in Figure 75 represents equilibrium position seen in Figure 63.

Solvent Breakthrough

An important aspect of the question of the effect of organic solvents on clay permeability is the breakthrough phenomenon which was observed in a number of solvent/clay systems. These

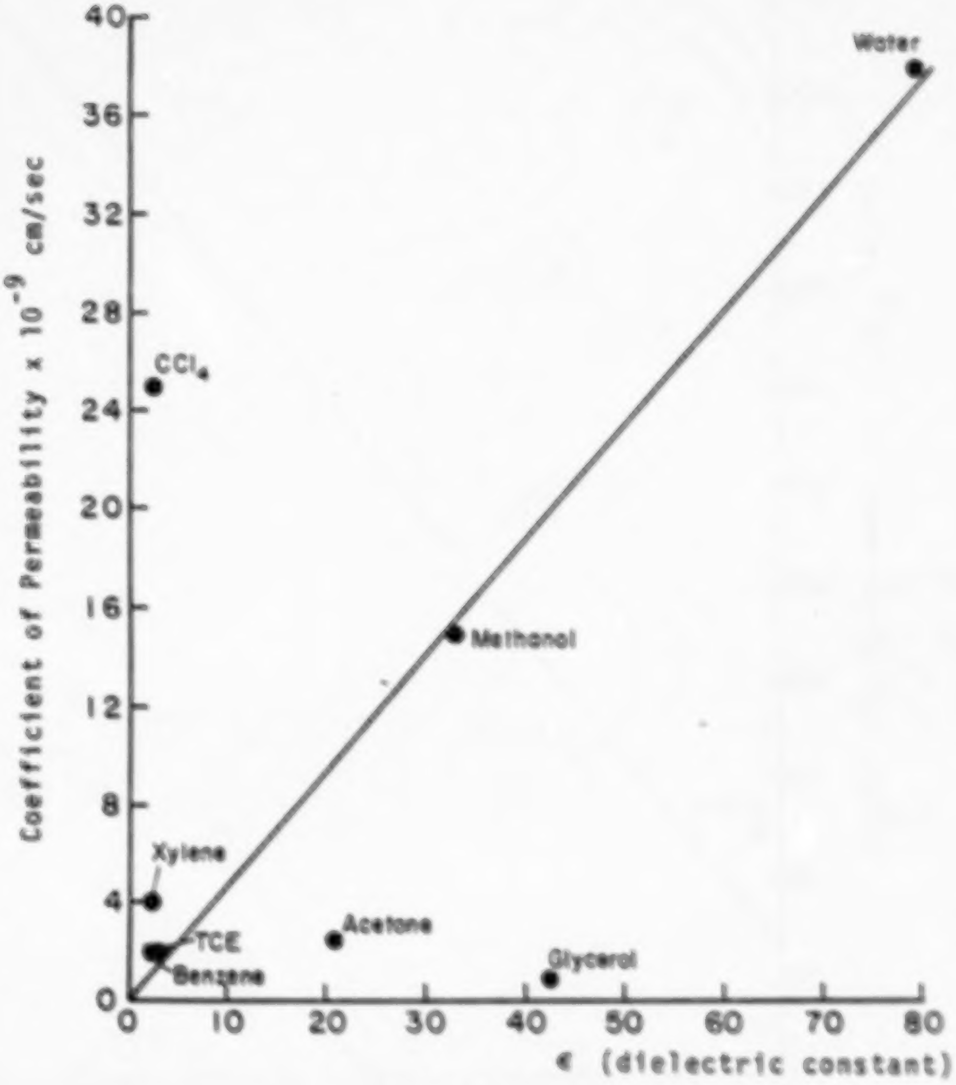

Figure 73. Relationship between coefficient of permeability and dielectric constant for solvents in Ranger Shale

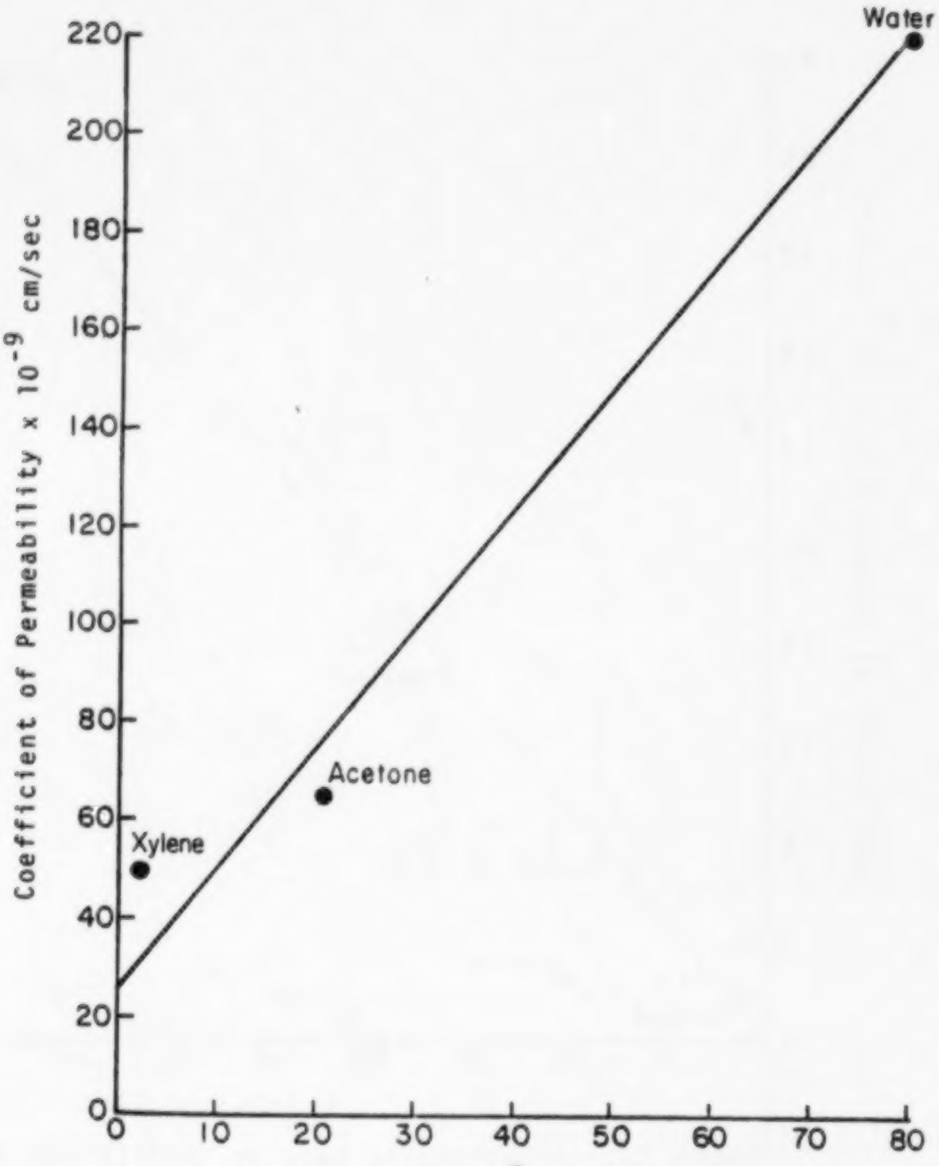

Figure 74. Relationship between coefficient of permeability and dielectric constant for solvents on Kosse Kaoline

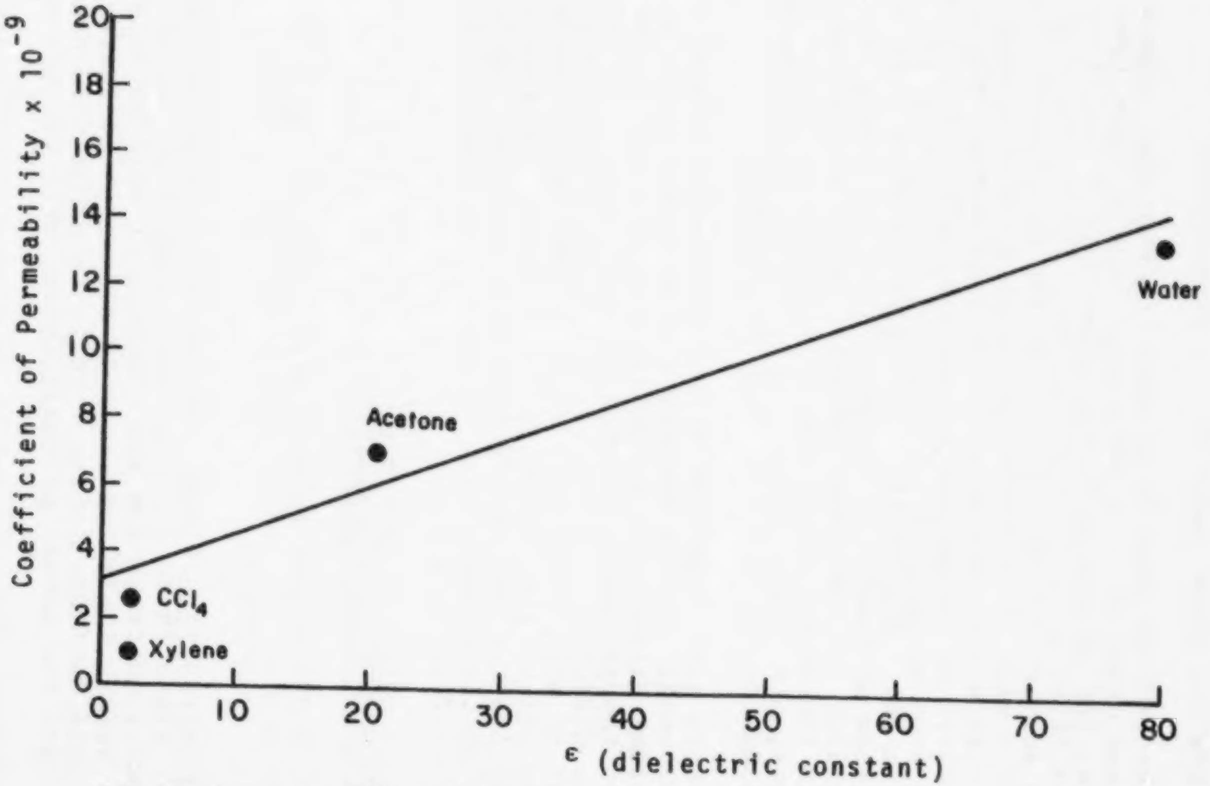

Figure 75. Relationship between permeability and dielectric constant for solvents on Fire Clay

cases were related to the fact that certain solvents caused the clay to shrink, thus forming channels through which the solvent could flow, in addition to migrating by convection in two unsuccessful runs with the permeability testing system, CCl_4 broke through Ranger Shale in six and eight days. After one breakthrough, fresh CCl_4 was poured onto the column and was observed to flow along the glass walls of the permeameter.

Another extreme case of solvent breakthrough caused by shrinkage was observed with benzene on Ranger Shale (see Figure 52). There, the permeability vs. time curve appeared to be normal for the first seven days of the run, but by the eighth day all of the solvent had drained out of the permeameter chamber. A less dramatic case of breakthrough occurred with xylene on Fire Clay (see Figure 63) when after 24 days of normal behavior, the coefficient of permeability rose precipitously over a four day period from an equilibrium value of 1×10^{-9} cm/sec to 45×10^{-9} cm/sec. Examination of Figure 28 shows that Fire Clay underwent slow shrinkage in xylene, and it is likely that this was responsible for the breakthrough. While initial shrinkage was seen in the Shrink-Swell tests conducted on Ranger Shale with benzene, the Ranger Shale - CCl_4 system showed about 1.1 percent swell during the first 10 days of exposure.

It can be concluded that any solvent which causes a clay to shrink appreciably during any stage of a shrink-swell experiment is a potential hazard when stored in a clay-lined disposal area. Even though such a solvent may move slowly through a wet clay by diffusion and convection, there is in principle a danger that it will eventually cause shrinking and cracking and thereby allow fluid transmission in bulk. Because of its obvious implication for the storage of commercial organic solvents in clay-lined pits, this is one of the signal observations to be derived from this study.

Properties of Clays of Potential Importance in Governing Permeability

Table 28 summarizes several properties of the clays investigated which might be influential in governing their permeability to solvents.

Montmorillonite Content: Montmorillonite is an expandable layer clay; exposure to liquids could cause swelling of individual montmorillonite grains and clogging of soil pores and channels. Ranger Shale was the only clay-soil evaluated that had measurable montmorillonite. While it might have been expected to have the lowest permeabilities, this was not observed.

Void Ratio: The void ratio, or volume of voids divided by volume of solids, ($e = V_v/V_s$) is generally acknowledged to be an important factor in determining permeability. (See, for example,

TABLE 28. CLAY-SOIL CHARACTERISTICS

Clay-Soil	Packed, Bulk Density lb/ft^3	Packed, Bulk Density g/cc	Percent Organic Carbon	Percent Montmorillinite	Void Ratio	K (x 10^{-9} cm/sec) For H_2O
Ranger Shale	108	1.73	0.28	4	0.4 -0.53	38
Kosse Kaoline	85	1.36	0.12	-	0.37-0.74	220
Fire Clay	113	1.81	0.03	-	0.19	13.5

Terzaghi and Peck (1948) and Amer and Awad (1974)). Based on void ratios, Ranger Shale should have been the most permeable clay, followed by Kosse Kaoline and then Fire Clay. The observed order was Kosse Kaoline > Ranger Shale > Fire Clay. Therefore, for the limited number of clays evaluated in this study, there was no correlation between void ratio and permeability.

Clay Density: Clay density, which is a function of mineral composition and packing, seems like a less fundamental parameter than void ratio and no correlation between this and permeability was anticipated prior to the experimental work. Yet, of all the properties considered, density appeared to be the one which correlated best with the observed data. The observed relationship was that as packed, bulk density increases, the permeability of the clay decreases. This is shown in Figure 76. (Later in this section of the report, an empirical equation is derived which relates permeability to clay density).

Permeability to Solvent Mixtures

Permeability data were obtained on four binary solutions containing acetone mixed with either benzene or carbon tetrachloride. The choice of solvent systems was based on the need for acquiring information on the behavior of mixtures, particularly those containing one component that causes clay shrinkage and another that causes swelling. Shrinkage can in principle bring about a rapid transmission of fluid through the clay and should be prevented at all costs, possibly by judicious mixing of solvents. This set of experiments was designed, in part, to test the effectiveness of such mixing in preventing breakthrough. Solution compositions and permeability coefficients for the solvent mixtures evaluated are listed in Table 29.

The acetone-benzene mixtures all had higher permeability coefficients than either of the pure components, but there appeared to be no correlation between permeability and solvent mixture composition. One likely explanation for the higher

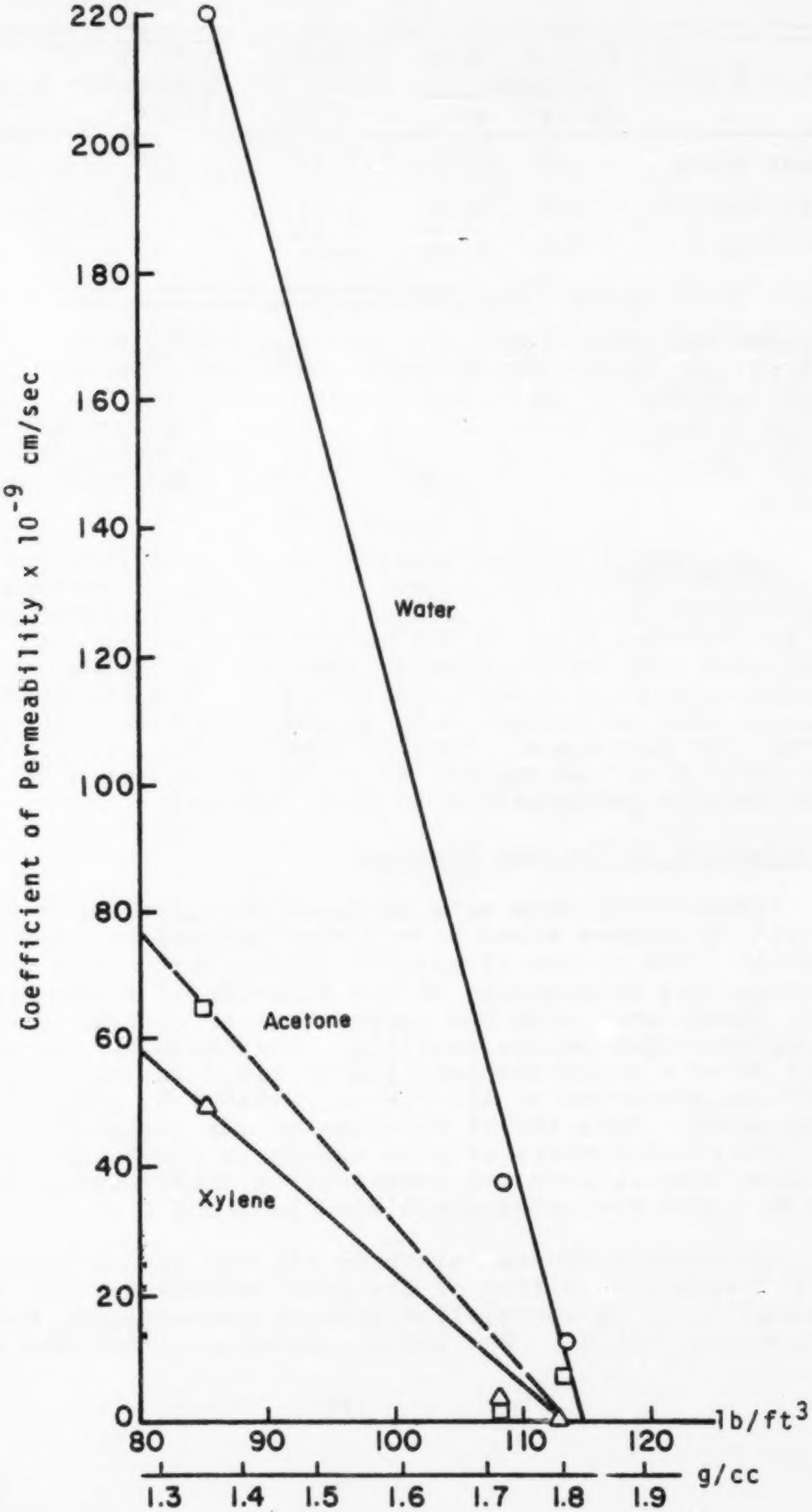

Figure 76. Coefficient of permeability as a function of packed bulk clay density

TABLE 29. COEFFICIENTS OF PERMEABILITY FOR FOUR BINARY MIXTURES

(with Ranger Shale)

System	K (x 10^{-9} cm/sec)
25 mole% acetone/ 75 mole% benzene	5.0
50 mole% acetone/ 50 mole% benzene	17.5
75 mole% acetone/ 25 mole% benzene	7.5
75 mole% acetone/ 25 mole% carbon tetrachloride	9.1
acetone	2.5
benzene	2.0 (before breakthrough)
carbon tetrachloride	25

permeability values follows from the earlier discussion of swelling. There it was noted that clays tend to behave selectively in their interactions with mixtures. Such selectivity probably comes into play during permeation as well, with one component of the mixture moving more rapidly than, and independently of, the other. Since acetone has the lower octanol/water partition coefficient it should migrate more quickly through the saturated pores of the clay. Thus the measured coefficients for the mixtures probably represent, to a large degree, the movement of acetone alone. This is entirely consistent with the view that the clay plug acts as a chromatographic column and partitions molecules according to their sorption behavior.

This, however, leaves unexplained the fact that mixtures have a higher permeability than acetone itself. One possibility is that the K value obtained for pure acetone is low because of the aforementioned microbial activity. For the mixtures, such activity would be prohibited by the bactericidal properties of benzene and carbon tetrachloride.

The most important observation, however, is that none of the mixtures, after a period of 36 days, underwent breakthrough as did pure xylene, benzene and, in two preliminary cases, pure carbon tetrachloride. This is significant, because it indicates that mixing two solvents in such proportion as to cause swelling (recall that the three mixtures being discussed all caused Ranger Shale to swell more than 5 percent) prevents breakthrough from occurring. Even though the coefficients of permeability are higher for the mixtures than the pure solvent, they are still quite low as compared with water.

For the mixture of acetone and carbon tetrachloride, the coefficient of permeability was markedly lower than for carbon tetrachloride alone. The lower value can be attributed to the fact that in this mixture the clay did not undergo shrinkage, so there was no possibility of leakage around the edges. Again, the measured permeability was due largely to the movement of acetone, and it was for this reason that the K value for the acetone/carbon tetrachloride mixture (75 volume percent/25 volume percent) closely approximated that for acetone/benzene (75 percent/25 percent).

Finally, it should be noted that the behavior of mixtures was, in general, quite similar to that of pure solvents, both in terms of the temporal variation in the permeability coefficient, and in terms of its magnitude. Based on an understanding of the behavior of the components, it is now possible to predict the coefficient of permeability for organic solvent mixtures. Based on the dielectric constants as shown in Table 20 and the findings shown in Table 29, a quaternary solution composed of equal amounts of benzene, xylene, carbon tetrachloride and methanol, would be expected to have a coefficient of permeability (using Ranger Shale) of 15 to 30 x 10^{-9} cm/sec, a somewhat higher permeability value than for methanol.

While there is considerable work to be done in the area of mixture permeability studies, this investigation has shown that an understanding of the basic properties of organic solvents and clays can, in principle, be used to predict the behavior of complex industrial wastes.

CONCLUDING REMARKS

The coefficient of permeability, one of the most important soil characteristics affecting contaminant transport from land disposal sites to groundwater, can have a wide range of values extending over many orders of magnitude. Terzaghi and Peck (1967) have summarized representative values which are presented in Table 30.

TABLE 30. COEFFICIENTS OF PERMEABILITY FOR TYPICAL SOILS

Soil Type	$K(\frac{cm}{sec})$	Comment
Course Gravel	$> 1 \times 10^{-1}$	Very Permeable
Sand or Fine Sand	10^{-1} to 10^{-3}	Medium Permeability
Silty Sand	10^{-3} to 10^{-5}	Low Permeability
Silt, Fine Sandstone	10^{-5} to 10^{-7}	Very Low Permeability
Clay	$< 1 \times 10^{-7}$	Impervious

After Terzaghi and Peck (1967).

K values as low as 2×10^{-10} cm/sec have been observed for some clays.

Based on this system of classification, Ranger Shale ($K = 38 \times 10^{-9}$ cm/sec for water) and Fire Clay ($K = 13.5 \times 10^{-9}$ cm/sec for water) are "impervious" and Kosse Kaoline ($K = 2.2 \times 10^{-7}$ cm/sec for water) has a "very low permeability." With respect to the organics studied, all of the soils are "impervious" since the highest coefficient of permeability obtained in this work for an organic solvent was 0.65×10^{-7} cm/sec for acetone on Kosse Kaoline.

The numerous equations which have been reported for predicting the permeability of porous media [e.g., Hazen (1911), Amer and Awad (1974), Terzaghi and Peck (1948)] have had limited applicability, and none have proved satisfactory for estimating fluid behavior in clays. The failure of the widely used Kozeny-Carman equation, shown below,

$$K = [1/(k_o T^2 S_o^2)] \quad [n^3/(1-n)^2] \quad [r/\eta] \qquad (40)$$

K = coefficient of permeability or hydraulic conductivity (cm/sec)
k_o = pore shape factor ($\sim$2.5)
T = tortuosity factor ($\sim \sqrt{2}$)
S_o = specific surface area per unit volume
n = porosity
r = viscosity
η = unit weight of pore fluid

has been discussed in detail by Mitchell (1976, p. 248) and considers largely the effect of unequal pore size in the clay. Mitchell has also noted that the permeability of a clay can be strongly influenced by molding water content and by method of compaction and that, in general, "properties of any given soil are dependent on structure to such an extent that analyses based on properties determined from the same material but with a different structure may be totally in error." The problem of predicting permeability is thus related to the considerable difficulties involved in adequately representing soil structure by a suitable parameter.

Ideally, the Kozeny-Carmen equation should be applicable to all permeants since the fluid viscosity and density are included as variables. However, the results of this study point out an additional problem, namely, that the permeability of a non-aqueous liquid does not depend on the ratio of density to viscosity as widely supposed but rather on the hydrophobic and hydrophilic character of the solvent. This hydrophobic/hydrophilic nature is best represented either by the logarithm of the octanol/water partition coefficient or by the dielectric constant. Any future efforts to develop a general permeability equation for the movement of liquids through a water-containing soil should take these into account.

The permeability data reported here were analyzed in the following way: It was assumed that the coefficient of permeability, K, was related to the dielectric constant, ε, by the equation

$$K = L\varepsilon^m \qquad (41)$$

m was the slope obtained by plotting log K vs. log ε for solvents on a given clay; L was a constant. For all three clays, m was estimated to be about 0.75.

Based on limited data, the density of the clay appeared to be the other significant variable and the dependence of K on density, d, was obtained from

$$K = Rd^n \qquad (42)$$

From a plot of log K vs. log d for each solvent, n, the slope, was determined to be approximately 7; R was a constant.

Finally, combining Equations 41 and 42, K was plotted against $\varepsilon^{0.75}/d^7$ on log-log paper (see Figure 77) and from the measured slope and intercept the empirical dependence of the coefficient of permeability on solvent dielectric constant and density was determined to be

$$\log K = 1.17 \, [\log (\varepsilon^{0.75}/d^7)] - 7.23 \qquad (43)$$

Table 31 presents calculated and observed values for the 11 single solvent systems which behaved in reasonable accord with the model discussed in this section. In general, the estimates of measured K values are quite good. The purpose of developing this equation was twofold:

1. It provides an empirical relationship between permeability and the two major variables found in the study and therefore acts as a summary of the permeability results for this work.

2. It calls attention to the important role which dielectric constant plays in determining permeability.

In its present form, this relationship cannot be used to predict permeabilities for any clay-solvent system. It is expected, for example, that it would not hold at moisture contents other than optimum, nor would it apply to the same clays compacted in a different way. In general, it summarizes too small a number of data points to be of significance other than as a prototype for equations incorporating dielectric constant.

A more empirical approach to predicting permeabilities of clay liners to hazardous organic wastes would be to obtain the permeability of the liner to water and then, using the results of this study, estimate the permeability of the clay to the waste. Based on the foregoing discussion, this could be accomplished using the equation

$$K_s = K_w \, (\varepsilon_s/\varepsilon_w)^{0.75} \qquad (44)$$

where K_s and K_w are the coefficients of permeability of the solvent and water, respectively, and ε_s and ε_w are the respective dielectric constants.

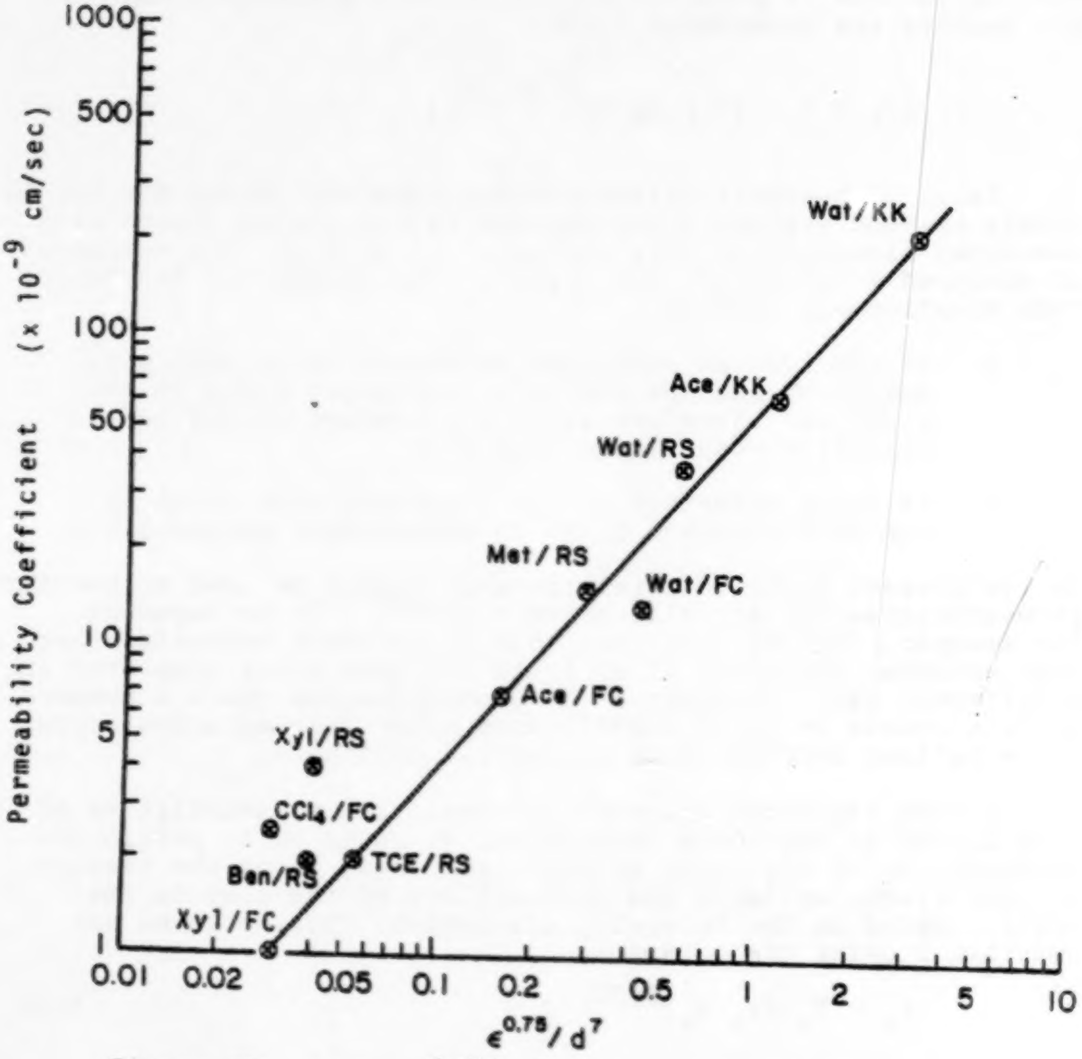

Figure 77. K vs. $\varepsilon^{0.75}/d^7$ for organic solvents and water on three clays

RS = Ranger Shale
FC = Fire Clay
KK = Kosse Kaoline

Ace = Acetone
Ben = Benzene
Met = Methanol
Wat = Water
Xyl = Xylene

TABLE 31. CALCULATED AND OBSERVED PERMEABILITY VALUES FOR ELEVEN SINGLE SOLVENT SYSTEMS

System	K_{obs} (cm/sec x 10^9)	K_{calc} (cm/sec x 10^9)
Ranger Shale		
Benzene	2.0	1.38
Xylene	4.0	1.40
Trichloroethylene	2.0	1.96
Methanol	15.0	14.0
Water	38.0	30.8
Kosse Kaoline		
Acetone	65.0	67.5
Water	220	219
Fire Clay		
Xylene	1.0	1.00
Carbon tetrachloride	2.5	0.98
Acetone	7	6.8
Water	13.5	22.2

The development of an equation which can be used to predict the permeability of any soil to any permeant is a formidable task and attempts to accomplish this have met with only limited success. The contribution of this study, in this regard, has been to point out the significance of permeant properties other than viscosity and density and to show how these might be used to estimate the permeability of soils to hazardous organic wastes. In addition, it has been shown that the ability of low dielectric liquids to dehydrate and shrink clays and to possibly cause them to transmit fluids more rapidly, adds a significant dimension to the problem of waste storage and containment. However, the results of mixture experiments indicate that the potential for breakthrough is greatly diminished or eliminated by the addition of a high dielectric liquid such as water.

The results point out the need for more laboratory studies to be undertaken on the effect of clay properties on the transmission of organic solvents. There is also a crucial need for field work to test the validity of the generalizations offered in this report. Until this has been carried out it will not be clear to what extent the conclusions drawn here actually apply to a real waste storage problem.

SECTION 7

SURVEY OF CURRENT PRACTICES FOR LAND DISPOSAL OF HAZARDOUS WASTES

INTRODUCTION

Shortly after initiating this study, it was decided that it would be informative to determine current state regulations and practices for land disposal of hazardous wastes. In late summer 1977, a letter was sent to each state's pollution control agency requesting a copy of the regulations governing land disposal of hazardous wastes. Specific information was requested on the handling of waste organic solvents, specifications for permeability of soils and/or liners (maximum permeability coefficients) for industrial waste disposal pits, methods for determination of permeability of soils and liners, and other information pertinent to land disposal of hazardous industrial wastes with a high organic solvent content.

Many of the states responded to the initial request during the fall and winter, 1977. Two additional follow-up requests were made to those agencies who had not responded to previous requests. By the spring of 1978 all states had responded. Several states indicated in their response that they were in the process of developing regulations pertinent to this area. Further, a number of states indicated that they were planning to review the US EPA's forthcoming criteria for land disposal of hazardous chemicals for adoption. These criteria were published in the December 18, 1978 Federal Register.

SUMMARY OF RESPONSES

Over three-fourths of the states did not, at the time of inquiry, have specific regulations or guidelines governing the land disposal of potentially hazardous wastes containing organic solvents. A number of states did not, at the time of inquiry, permit the disposal of hazardous wastes of this type within the state. Several states also responded that no regulations were needed within the state. Many states indicated that they approached land disposal of hazardous waste on a case-by-case basis but did not provide any guidelines or other information upon which they based their decision about the suitability of a disposal site or wastes permitted to be disposed. Many states indicated that they required monitoring of disposal sites but did not specify the characteristics of the monitoring program that should be followed.

Of particular pertinence to this study, is that only 11 states specified a maximum permeability for clay liners or the soils in the region of the disposal area. The specified values ranged from 10^{-5} cm/sec for soils in their natural state (Michigan) to California's and Oklahoma's values of 10^{-8} cm/sec. Most frequently a maximum permeability of 10^{-7} cm/sec was specified. None of the states specified the procedures that were to be followed in determining the coefficient of permeability. Texas was the only state that specified that some of the waste material should be tested, however no specific guidance was given on how this should be done.

A wide variety of soil types and liner thickness were being permitted for use in disposal areas. There seemed to be little or no concensus about appropriate soil types or thickness of soil liners.

From an overall point of view, it appears from the results of this survey that most states have not developed specific criteria for such parameters as soil type, liner permeability and thickness, and methods of measurement of permeability as they apply to hazardous waste disposal site selection. The US EPA in the December 18, 1978 Federal Register proposed a soil permeability of not less than 10^{-7} cm/sec. They do not, however, specify the procedure for determination of permeability. This is a significant omission in that many of the standard permeability tests that are used can not be performed satisfactorily in the presence of organic solvents. It is evident from this survey that there is an immediate need for evaluating the significance of organic solvents in affecting the ability of industrial waste disposal pits to retain hazardous wastes.

Since the initiation of this study, there has been a general public and legislative awakening to the potential and real hazards of land disposal of some types of industrial wastes. This increased awareness has further increased the need for work in this area.

A synopsis of the information obtained from the states as well as a synopsis of portions of the December 18, 1978 Federal Register pertinent to this project have been submitted to the US EPA-Ada as a separate set of Appendices to this report. Copies are available from the Robert S. Kerr Environmental Research Laboratory upon request.

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Appendices are available from the authors upon request.